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INORGANIC SEMINAR ABSTRACTS

1963-64

Department of Chemistry and Chemical Engineering

University of Illinois

INORGANIC SEMINAR ABSTRACTS

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SUMMER 1963

Department of Chemistry and Chemical Engineering

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RECENT STUDIES ON UNSYMMETRICALLY DELOCALIZED
PI-BONDED AND SIGMA-BONDED HYDROCARBON
TRANSITION-METAL COMPLEXES USING NUCLEAR
MAGNETIC RESONANCE

B. W. Baylis

July 11, 1963

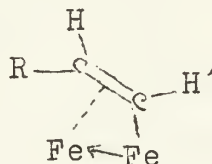
Only during the last ten years has there been much research in organometallic chemistry. Before the accidental discovery of ferrocene in 1951 there were only a few transition metal complexes containing a metal to carbon bond. The discovery of such a radically different complex which was so stable stimulated considerable interest in this field. By 1955 the organometallic literature was sufficiently extensive for Cotton to write a lengthy review (1) in which he stated that there were no cyclopentadienyl complexes containing a localized carbon to metal sigma bond. Within a year, however, well-substantiated examples of cyclopentadienyl-metal sigma bonds were in the literature (2). There are, in addition to these sigma bonds and the "sandwich"-type bonds of ferrocene, three classes of bonds that have been shown to exist between metals and ring systems. These are the olefin-type, which involve the donation of electrons of a single π bond to the metal, the unsymmetrically delocalized type, and the essentially electrostatic attraction of the metal cation for an anion. Sodium, magnesium, scandium, yttrium, and the rare earth cyclopentadienides belong to this class. A recent mode of attachment to come to light is the allyl type, in which the metal is bonded to three carbons through a delocalized π cloud. The determination of type of bonding in a given complex poses a special problem. Even x-ray crystal studies have not given any ultimate proof of bonding type, since a given structure could be caused, in some cases, by more than one type of bonding (3). Then, too, determining the position of a carbon atom in the vicinity of a large metal ion requires especially accurate work. Studying chemical properties is often an excellent way to look at bonding, but this approach has a great number of problems associated with it. Many erroneous structures have been proposed on the basis of chemical reactivity (3,4,5,6) although it must be said that the chemical properties of an equal number of complexes caused the rejection of erroneous structures proposed on other bases (3,7,8).

One of the relatively successful physical methods has been nuclear magnetic resonance. This started being used as an analytical tool in 1954 and its use has steadily increased since then. In 1956 Piper and Wilkinson used n.m.r. in determining the structure of some of the first sigma complexes(9). Some examples of recent work utilizing n.m.r. follow.

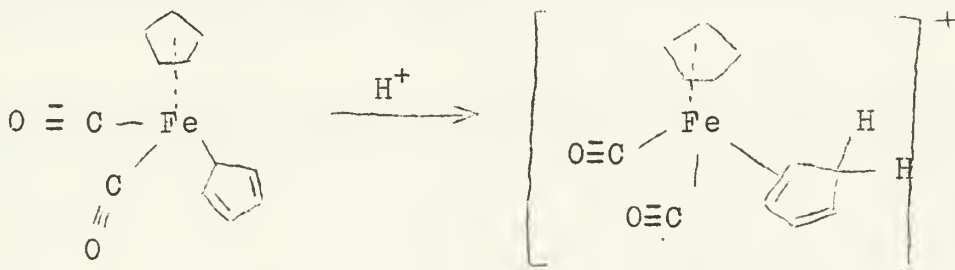
Many alkyl-metal complexes have been investigated but the results of King's work on compounds of the type

$\text{Fe(CO)}_2 - (\text{CH}_2)_n - \text{Fe(CO)}_2$ were the most unexpected(10). He varied n from 3 to 6 and obtained a single, sharp resonance for the alkyl hydrogens in each case. These peaks occurred at 1.42, 1.35, 1.40, and 1.36 ppm* for $n = 3, 4, 5$ and 6, respectively. The phenomenon of loss of splitting caused by exchange is well known, but mere hydrogen exchange could not explain this spectrum. Hence, if any exchange is occurring, it must equilibrate the carbons in some way.

King has also studied a case where an olefin is π bonded to one iron and σ bonded to another:



He assigned the doublet at 8.90 ppm to H' and the one at 5.40 ppm to H . Green studied the product in the reaction

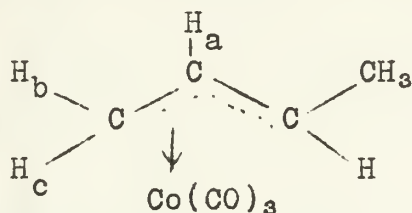


and assigned the resonance at 3.44 to the CH_2 and the complex band with centers at 6.5 and 5.7 ppm to the olefinic hydrogens(12). Two diolefins that have been studied are $\pi\text{-Cp-Co-C}_8\text{H}_8$ and $\pi\text{-CpRhC}_8\text{H}_8$ (13). These contain two free olefins and two olefins bonded to the metals through localized bonds. The band at 5.44 (5.53 for Rh) was assigned to the free olefinic protons and the one at 3.50 (4.06 for Rh) to the protons on the bonded olefins. The π -cyclopentadienyl cobalt complex of cyclooctatriene, in which only one olefin is not bound gave similarly placed bands, at 5.38 and at 3.54, plus another stretching from 2.8 to 1.5 due to the methylene protons (14).

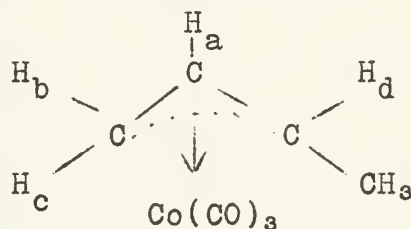
Several allyl type complexes have been studied. Green looked at $\text{CpFe(CO)}_2\text{CH}_2\text{-CHCH}_2$ and reported some of the peaks but made no assignments (15). He also studied $\text{CpMo(CO)}_2\text{CH}_2\text{CHCH}_2$ and assigned the quadruplet at 3.28 to the central proton, the

* All chemical shifts are reported in ppm with respect to tetramethylsilane.

doublet at 0.87 to the terminal hydrogens trans to the central one, and the quadruplet at 2.60 to the terminal hydrogens cis to the central proton (16). An earlier paper by Chien and Dehm on palladium complexes of allyl derivatives gives detailed spectra and assignments (17). More recently Bertrand et al. looked at Co-tricarbonyl complexes of allyl derivatives and reported the following spectra: (18) (See page following)

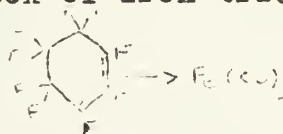


Isomer I

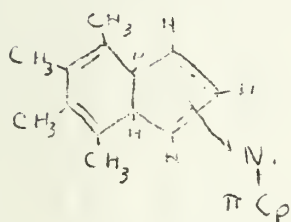


Isomer II

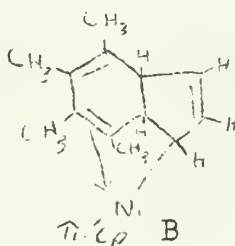
Wilkinson's study on the complex of iron tricarbonyl with C_6F_6 indicated an allyl-type bond: (19)



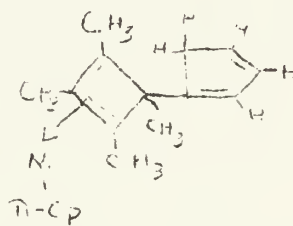
King studied the nickel complex previously given the structure A



A



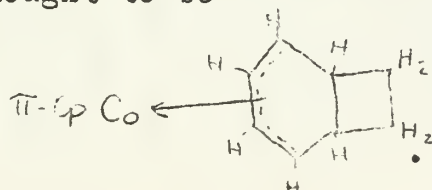
B



C

and suggested structure B on the basis of its n.m.r. spectrum which gave four different methyl resonances (6). He made no attempt to assign the other peaks in the spectrum. Dahl's x-ray work indicates structure C.

Many butadiene-type complexes have been studied. In the $CoCp_2H$ complex the cobalt was found to be bound to the second cyclopentadiene by this type of attachment (20). The cobalt cyclopentadienyl complex of 1,3,5 cyclooctatriene gave an expected butadiene-type bond, but no resonance was noted typical of a free olefinic hydrogen (21). The structure was therefore thought to be



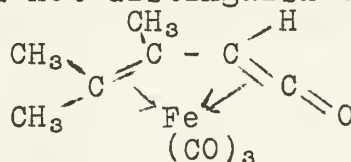
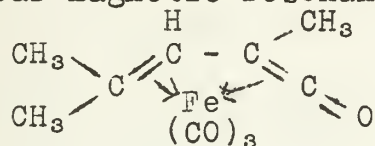
Chemical Shifts

Coupling Constants in Cycles per Second

	H _a	H _b	H _c	H _d	CH ₃	CH ₃ ¹
1-Me π -allyl I	5.37	3.45	2.62	3.79	2.17	...
1-Me π -allyl II	5.62	3.92	3.47	4.89	...	1.82
1,1-Me ₂ π -allyl	5.37	3.70	3.15	...	2.39	1.92
1,1,2 Me ₃ π -allyl	...	3.77	3.29	2.60 (2-Me)	2.45	1.95
1,3-Me ₂ π -allyl I	5.20	...	3.45	3.45	2.19	...
1,3-Me ₂ π -allyl II	5.42	...	3.52	4.50	2.29	1.82
1-Et π -allyl I	5.37	3.57	2.58	3.65	...	1.77
1-Et π -allyl II	5.53	3.89	3.39	4.82	1.55	...

J _{ab}	J _{ac}	J _{ad}	J _{bc}	J _{bd}	J _{Hd-CH₃}
6.3	10.5	10.5	<0.2	<0.2	6.5
7.1	12.3	6.8	0.6	1.6	7.0
6.4	11.2	...	1.2
...	0.8
...	9.8	9.8	6.5
...	11.3	7.2	6.5, 6.5
6.2	10.4	10.0	<0.2	<0.2	6.3
6.4	10.9	7.0	0.8	1.6	6.3

The cyclohexadiene complex gave a similar resonance at 4.80 ppm (5.04 in the bicyclo derivative) which was assigned to the butadienyl hydrogens. The iron tricarbonyl complex of the same cyclooctatriene did give a free olefinic hydrogen resonance which overlapped with two of the bound olefinic hydrogens (14). Another six-membered ring found to have butadienyl bonding by n.m.r. was the octafluorocyclohexadiene derivative of iron tricarbonyl (22). A product of the reaction between triiron dodecacarbonyl and 1,3,3 trimethylcyclopropene was found to have one of the following two structures. Nuclear magnetic resonance could not distinguish between them (23).



Pentadienyl bonding has been well studied in the form of cyclopentadienyl complexes. A somewhat surprising variation in chemical shifts for these protons has been observed. There are a few cases of this type of bonding where the ring itself has more than five carbons. For example, the products of protonation of cycloheptatrienyl and cyclooctatrienyl iron tricarbonyl appear to contain seven membered rings, five of whose carbons are donating four electrons to the iron (13,24). The bonding in cyclooctatetraenyl iron tricarbonyl is problematic since it gives only one proton resonance yet x-ray has shown that a coplanar unit of four of the carbons are near the iron, the rest being farther away (25). Doubtless some sort of exchange phenomenon is operative here.

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PRINCIPLES AND APPLICATIONS OF THE NMR DOUBLE RESONANCE TECHNIQUE

H. F. Henneike

July 23, 1963

I. INTRODUCTION

The NMR double resonance was first suggested by Bloch (22). Bloch (19) and Bloom and Shoolery (20) have worked out the detailed theory involved. In existence less than ten years the technique has been put to various uses.

- 1) Measurement of the Larmor frequency of a nucleus when an oscillator for detecting the resonance of this nucleus is not available.
- 2) Measurement of chemical shifts of nuclei with small magnetogyric ratios where signal to noise ratio is poor.
- 3) Measurement of chemical shifts for protons that are obscured by overlapping features of other protons in the molecule or by solvent resonances.
- 4) Measurement of the amplitude of an applied r.f. field.
- 5) Measurement of small relative chemical shifts in molecules where nuclei are nearly equivalent.
- 6) Measurement of relaxation times and exchange rates.
- 7) Determination of the relative signs of coupling constants in first order spectra of spin systems including at least three magnetically non-equivalent spins (AKX etc.).
- 8) Simplification of spectra through spin decoupling, removal of quadrupole broadening, and determination of correct spin-spin coupling assignment.
- 9) Nuclear-electron double resonance to increase greatly the intensity of an NMR line through nuclear polarization.

II. THEORY

The double resonance experiment is performed by applying a strong oscillatory field H_2 of frequency ω_2 near the resonance frequency of one type of nucleus (to be decoupled). Transitions of other nuclei in the spin system are then investigated with a weak oscillatory field H_1 of frequency ω_1 . H_2 is strong and H_1 weak in the sense that

$$(\gamma_2 H_2)^2 T_1 T_2 \gg 1 \quad [1]$$

$$(\gamma_1 H_1)^2 T_1 T_2 \ll 1 \quad (23) \quad [2]$$

The total magnetic field H for a double resonance experiment consists of the usual strong static magnetic field H_0 in the z direction, the usual oscillatory investigating field in the xy plane H_1 and the added strong oscillatory field H_2 in the xy plane.

$$H = (H_1 \cos \omega_1 t + H_2 \cos \omega_2 t) \hat{i} - (H_1 \sin \omega_1 t + H_2 \sin \omega_2 t) \hat{j} + H_0 \hat{k} \quad [3]$$

The Hamiltonian for a molecule in a liquid state in the field is

$$H = H^0 + H^1(t) \quad [4]$$

$$H^0 = - \sum_i \frac{\gamma_i H_0}{2\pi} I_z(i) + \sum_{i,j} J_{ij} I(i) \cdot I(j) \quad [5]$$

$$H^1(t) = - \frac{\gamma_i H_2}{2\pi} [I_x(i) \cos \omega_2 t - I_y(i) \sin \omega_2 t] - \frac{\gamma_i H_1}{2\pi} [I_x(i) \cos \omega_1 t - I_y(i) \sin \omega_1 t] \quad [6]$$

γ_i = magnetogyric ratio of nucleus i including the chemical shift
 J_{ij} = spin-spin coupling constant between nuclei i and j (cps.)

Since H is time dependent it is not possible to derive time independent solutions to the appropriate Schrödinger equation. However the time dependent portion of H due to H_2 can be removed if we transform our coordinate system to one rotating with angular velocity $\omega_2 \hat{k}$. (20)

Letting the subscript R denote functions in the rotating system we have

$$\psi_R = \exp \left(\frac{i}{2} \omega_2 I_z t \right) \psi \quad [7]$$

$$i \frac{\partial}{\partial t} \psi_R = 2\pi \mathcal{H}_R \psi_R \quad [8]$$

$$\mathcal{H}_R = \mathcal{H}_R^0 + \mathcal{H}_R^1(t) \quad [9]$$

$$\mathcal{H}_R^0 = \sum_i \left[- \frac{\gamma_i H_0}{2\pi} + \frac{\gamma_i \omega_2}{2} \right] I_z(i) + \sum_{i,j} J_{ij} I(i) \cdot I(j) \quad [10]$$

$$\mathcal{H}_R^1(t) = - \frac{\gamma_i H_1}{2\pi} [I_x(i) \cos (\omega_1 - \omega_2)t - I_y(i) \sin (\omega_1 - \omega_2)t] \quad [11]$$

Assuming now that $\mathcal{H}_R^1(t) \ll \mathcal{H}_R^0$, [8] can be solved by first order perturbation theory.

For the particular case of an AX system, both A & X having spin $\frac{1}{2}$, \mathcal{H}_R is given by

$$\mathcal{H}_R = \left[\frac{1}{2\pi} \left(-\gamma_A \vec{H}_0 + \omega_2 \right) I_z(A) - \frac{\gamma_A \vec{H}_2}{2\pi} I_x(A) \right] + \left[\frac{1}{2\pi} \left(-\gamma_X \vec{H}_0 + \omega_2 I_z(X) - \frac{\gamma_X \vec{H}_2}{2\pi} I_x(X) \right) \right] + J_{AX} I(A) \cdot I(X) \quad [12]$$

For the decoupling field H_2 of large magnitude & frequency ω_2 near $\gamma_X H_0$, the X nucleus is quantized mainly in the X direction and the A nucleus along the z axis. The scalar product spin-spin coupling is then vanishingly small causing collapse of the spin multiplet of nucleus 1 due to spin of nucleus 2. (24)

It can be shown (20) that the energy levels in the rotating frame are given by

$$E(m_1, m_2) = \frac{1}{2} m_1 (\gamma_1 H_0 - \omega_2) + m_2 (\gamma_2 H_0 - \omega_2 + m_1 J) \cos \theta + m_2 \frac{1}{2} H_2 \sin \theta \quad (m_1) \quad [13]$$

m_1 = Z component of spin of nucleus 1

m_2 = nucleus 2 spin component in direction of its effective field (essentially X direction)

For the special case $I_1 = I_2 = \frac{1}{2}$ there are four possible transitions of which only two are allowed when $H_2 = 0$. When $H_2 > 0$ then all four transitions are observed because the angle between m_1 and m_2 changes during the transitions (i.e. the final m_2 state is not orthogonal to the initial m_2 state).

In the general case (including $I = \frac{1}{2}$), spin-spin multiplets in the absence of H_2 contain $(2I_2 + 1)$ lines. When H_2 is applied the selection rule ($\Delta m_2 = 0$ in the lab frame) no longer strictly holds, and in addition transitions starting from different m_1 levels may no longer be superimposed since eq. [13] is not linear in m_1 . Therefore there may be as many as $(2I_1)(2I_2 + 1)^2$ lines in the multiplet when H_2 is present. (20)

The multiplet structure then can become very complex. The situation is saved by the fact that for large values of ω_2 or J_{AX} , ω_2 very near the Larmor frequency of nucleus 2 the result agrees with that obtained by using the concept of an "averaging out" of the spin-spin interaction due to rapid transitions in the laboratory frame.

At intermediate values of ω_2 or J_{AX} , ω_2 far from $\gamma_X H_0$ the behavior of the spectrum is quite different from that expected from saturation of the nuclei decoupled. (25)

The multiplet structure varies as a function of the experimental method used. The methods most commonly employed are

1) $H_2 = H_0$, $H_0 = \text{constant}$, H_1 and H_2 variable

1a) H_2 variable through $H_2 = H_0$

2) $H_2 = H_0$, $H_1 = H_0$, and a sweep field ($H_0 + H_1$) used to investigate the spectrum

If we label the four transitions of the 2 spins $\frac{1}{2}$ case as a,b,c,d, the spectral behavior under each set of conditions can be summarized as

$$1) E_{(+,+)(-,+)} + E_{(-,-)(-,+)} = E_a; E_b = E_{(+,-)(-,+)} + E_{(+,-)(-,+)} \quad [14]$$

$$E_{(+,+)(-,-)} + E_{(+,-)(-,+)} = E_c; E_d = E_{(+,-)(-,+)} + E_{(+,-)(-,+)} \quad [15]$$

$$\begin{aligned} E_a &= E_b = H_0 + \frac{1}{2}J^1 \\ E_c &= H_0 + \frac{1}{2}J^1 \\ E_d &= H_0 - \frac{1}{2}J^1 \end{aligned} \quad [15]$$

$$J^1 = (J_{AX}^2 + J_{BX}^2)^{\frac{1}{2}} \quad [16]$$

and the relative probabilities are given by

$$P_a = P_b = \frac{J^1}{(J^1)^2} \quad [17]$$

$$P_c = P_d = \frac{J_{AX}^2}{(J^1)^2} \quad [18]$$

$$H_2 = 0$$



$\Delta H =$

1a

F^{19} spectra for $NaPO_3F$

2 Substituting $\nu_0 + \Delta H$ for ν_0 in eq. [13] and solving for $\Delta E = h\nu_1$ we find lines at (23)

$$\Delta H = 0$$

$$\text{with } P = \frac{\gamma_2^2 H_2^2}{(J^1)^2} \quad [19]$$

and at

$$(\Delta H)^2 = \frac{\pi^2 J^2 (\gamma_1^2 - \gamma_2^2) + \gamma_1^2 \gamma_2^2 H_2^2}{\gamma_1^2 (\gamma_1^2 - \gamma_2^2)} \quad [20]$$

$$\text{with } P = \frac{\pi^2 J^2}{(J^1)^2} \quad [21]$$

These results show that as H_2 increases a central component ($\Delta H = 0$) will appear and original doublet will spread out and fade if $\gamma_1 > \gamma_2$. If $\gamma_1 < \gamma_2$, they will collapse to single line for $\gamma_2 H_2 \geq J$. These results are then the same as for 1 and 1a. In each case results are the same in the limit $\Delta H = 0$, $\gamma_2 H_2 \gg J_{AX}$.

Such calculations as these are only approximations since they totally disregard relaxation mechanisms. The detailed rigorous treatment is by way of statistical quantum mechanics (26) (27). Such a treatment is truly complicated.

The detailed treatment does predict several additional interesting observables such as negative intensity signals in certain cases and, for a single spin ($\frac{1}{2}$) under double irradiation, the existence of two resonance frequencies. It also predicts a small residual separation of lines in the collapsed multiplet.

III. APPLICATIONS

A. Determination of amplitude of an applied r.f. field

The density matrix formalism of Bloch predicts the presence of two

resonance signals for a sample containing a single set of equivalent spin nuclei under double irradiation. (19)

for $m_s(-\frac{1}{2} - \frac{1}{2})$

$$+ = \omega_2 + [(\omega_s - \omega_2)^2 + \frac{J^2}{4}]^{\frac{1}{2}}$$

for $m_s(\frac{1}{2} - \frac{1}{2})$

$$- = \omega_2 - [(\omega_s - \omega_2)^2 + \frac{J^2}{4}]^{\frac{1}{2}}$$

$$+ - = 2[(\omega_s - \omega_2)^2 + \frac{J^2}{4}]^{\frac{1}{2}}$$

$$(+ -)^2 = 4(\omega_s - \omega_2)^2 + J^2$$

Anderson (14) determined $(\omega_s - \omega_2)$ with an audio oscillator and measured $(+ -)$ on successive traces of an H_2O system under double irradiation. Plotting $(\omega_s - \omega_2)^2$ versus $(+ -)^2$ gave $(\frac{J}{2})^2$ as the x intercept. Since J for proton is known this allowed direct calculation of ω_2 .

B. Relative Signs of Coupling Constants

In the absence of double irradiation a spin system containing at least three non-equivalent groups of nuclei must show some second order effects for analysis to yield the relative signs of the coupling constants. The analysis can be long and difficult.

Through use of the d.r. technique first order spectra can be made to yield information on relative signs of coupling constants directly.

In water solution the CH_2 and CH_3 multiplets of the diethyl thallium cation (Et_2Tl^+) are split into doublet groups by the Tl nucleus. The spectrum consists of two outer CH_3 triplets and two inner CH_2 quartets (1,2).

By irradiation at the center of gravity of each of the multiplets it was shown that each CH_3 triplet was coupled to the distant CH_2 quartet and vice-versa. This indicated that the $J_{Tl - CH_3}$ and $J_{Tl - CH_2}$ coupling constants were of opposite sign since for the same signs one would expect the two high field multiplets to be coupled together and the same for the two low field multiplets.

The results gave:

$$J_{Tl - CH_3} = \pm 628 \text{ cps.}$$

$$J_{Tl-CH_2} = \mp 340 \text{ cps.}$$

Their relative magnitudes agree with those for the ethyl lead and mercury compounds.

C. Removal of Quadrupole Broadening of Al^{27} and B^{11}

Spin multiplets may have their components severely broadened up to the point of collapse into one broad peak or even apparent decoupling if the second coupled nucleus possesses an electric quadrupole moment so that part of its spin-lattice relaxation arises from fluctuating electric field gradients.

In the H^1 spectrum of aluminum borohydride (AlB_3H_{12}) there is only one broad peak due to nuclear quadrupole broadening by both $^{31}_{12}Al^{27}$ (spin 5/2) and B^{11} (spin 3/2). The B^{11} irradiated H^1 spectrum ($H^1 - B^{11}$) is also a broad flat single peak. The $H^1 - Al^{27}$ spectrum is identical to that for a simple borohydride. The B^{11} spectrum is a symmetrical quintet (13).

These spectra show that all of the protons in a molecule are equivalent and that they are all coupled to both Al and B nuclei, also each B nucleus is coupled to four equivalent protons.

The authors were unable to reconcile these conclusions and other infrared and raman data (8) (9) with a single static model.

The temperature invariance of spectra and the narrow range allowed for exchange rates seemed to preclude a BH_4^- exchange or rotation process leading to the equivalence of all protons.

The authors proposed a non-classical "tunnel effect" penetration by the proton system. The temperature independence of spectra can be explained in this manner and further experiments with $Al(BHD_2)_3$ also seem to support their conclusions.

D. Removal of Quadrupole Broadening due to N^{14}

1. The quadrupole broadening in the uncoupled spectrum of pyrrole renders the NH proton signal undetectable. After decoupling the NH proton resonance appears as a quintuplet. The α and β protons appear as quartets in both spectra but are sharpened somewhat in $H^1 - N^{14}$ spectrum (6).

From measurements of μ and χ along with the known anisotropy effects of aromatic rings the authors decided on a "closed" rather than "open" hydrogen bonded dimer. They concluded that the bonding was of the π type with $K_{330} = 4.3$ mole fract.⁻¹

Similar studies on a pyrrole-pyridine system led to the conclusion that association here was largely n-type donation of the pyridine N free pair although there was some evidence for a second equilibrium involving a π complex, either pyrrole-pyridine or pyrrole-pyrrole. The equilibrium constant and enthalpy values agreed well with those from I.R. studies (28).

I.R.

NMR

$$K_{30} = 22 \pm 3$$

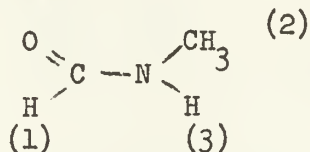
$$K_{23} = 23.1$$

$$\Delta H = -3.8 \pm 0.2 \text{ kcal/mole}$$

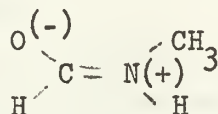
$$\Delta H = -4.3$$

2. In the normal H^1 spectrum of N-methyl formamide, the NH and CH resonances both appear as low broad single peaks. In the H^1 - N^{14} spectrum both peaks are sharpened and both now show structure (5). The CH peak is a quartet while the NH peak seems to be a partially unresolved quartet. The CH_3 resonances are unaffected by N^{14} decoupling. The sharpening of the CH resonance is taken as evidence for N-C-H coupling. Since such coupling is not usually observed unless there is some N-C double bonding this is taken as evidence for such.

Analysis of the spectrum as an ABX_3 system leads to the magnitudes and some of the relative signs of the coupling constants



H_2O dilution of N-methyl formamide leads to an increase in J_{13} (see above) and increased structure in the CH resonance. This suggests increasing N-C double bond character in H_2O solution. i.e.



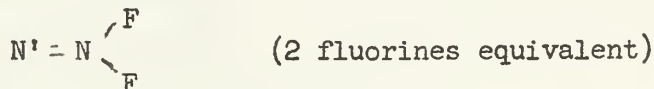
E. Determination of Type of Spin System Present

Samples of difluoro diazine prepared by thermal decomposition of N_3F or electrolysis of molten ammonium bifluoride contain two isomers differing greatly in their chemical reactivity and boiling points. (32)

Electron diffraction, I.R. and mass spectral studies agreed on the trans structure for the less reactive higher boiling isomer. I.R. studies seemed to indicate the 1,1-difluoro structure (32,33) while the other methods suggested the cis isomer.

Noggle and Baldeschwieler (11) obtained the F^{19} spectra for both isomers and carried out a detailed analysis. The spectra for both isomers were nearly identical. That for the trans isomer was analyzed successfully as an $AA'XX'$ case.

If the second isomer were



it could be either an A_2MX , A_2XY , or an A_2XX' spin system. For an A_2MX system one would expect a simple 9 line spectrum, all lines of equal intensity (A spectrum). This is not observed.

If the double resonance spectrum of an $AA'XX$, A_2MX or A_2XX' system is recorded by sweeping the magnetic field, the resonance of the A part of the

spectrum will be symmetric when $\nu_2 = -\nu_1$ (29,30). At equal frequencies above and below ν_0 the A resonances will be mirror images. This theory was applied to the ^{19}F - ^{14}N spectrum of the "cis" isomer for various values of $(\nu_2 - \nu_1)$ ranging from -312 cps to + 312 cps. The inversion expected for an A_2XX' or an $AA'XX'$ spectrum was noted.

An A_2XX' system does not seem very likely for the 1,1-difluoro isomer since the N and N' shielding should be very different. Furthermore spectra calculated on an IBM 7090 for various values of

$$\begin{aligned} J_{NF}, J_{NN} \\ J_{N'F}, J_{N'N} \end{aligned} = \begin{aligned} J_{N-F} \\ J_{N'-F} \end{aligned}$$

did not fit at all.

Both spectra can be fit by the same basis functions C_{2V} and line assignments if they are taken as $AA'XX'$ cis-trans cases. This work seems to be good evidence for the cis structure for the more reactive isomer.

F. Nuclear-Electron Double Resonance

In this only recently developed application of the general double resonance technique, a spin system containing both nuclear and free electron spins is irradiated over its electron resonances (microwave region) and the nuclear resonances are observed.

Because of the nucleus-electron magnetic coupling the populations of the nuclear energy levels are not independent of the populations of the electron energy levels. The nuclear spectrum can either increase, decrease or invert in intensity due to this induced nuclear polarization (Overhauser effect) depending on the nature of the nuclear-electron coupling and the relaxation processes of the system.

The intensity can be calculated to change by a factor

$$\frac{\gamma_e}{\gamma_N} \left(1 - \frac{T_1}{T_{10}} \right)$$

= -1/scalar n-c coupling)

(= $+\frac{1}{2}$ (dipolar n-c coupling)

γ_i = magnetogyric ratio of particle i

T_1 = nuclear spin lattice relaxation time in presence of paramagnetic species

T_{10} = nuclear spin lattice relaxation time in absence of paramagnetic species.

Actual applications are still very rare; however, it has been used to successfully enhance proton and fluorine resonances by a factor of 20X or more.(35) It has also been used to determine the relative strengths of H^1 -e and F^{19} -e dipolar couplings in solutions of fluorinated alcohols and 2,5-di-t-butyl-semiquinone. (36)

IV. CONCLUSION

The continued rapid growth of NMR double resonance techniques seems assured by

- A. Applications are as varied as NMR itself
- B. Commercial instrumentation is now available
- C. Double resonance methods of determining spin-spin coupling assignments are stronger proof than spectrum analysis and usually simpler
- D. The discovery of new applications is still continuing.

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FLUORINE COUPLING CONSTANTS-THEORY AND APPLICATION

David Herlocker

July 30, 1963

INTRODUCTION:

Gutowsky et al (1) and Hahn and Maxwell (2) were among the first to observe and explain the phenomenon which is today known as the coupling constant. It was determined that molecules such as PF_3 and PF_5 yielded doublets in the F^{19} spectrum. Although the PF_5 splitting had originally been interpreted as a type of chemical shift between different types of fluorine atoms, further studies have indicated the magnitude of the separation to be both field and temperature independent, in marked contrast to the previously studied chemical shift. Early work by Quinn and Brown (3) determined the same behavior for HPF_6 and $\text{FPO}(\text{OH})_2$. In these early studies, it was also determined that equivalent nuclei would not split one another, and also that nuclei possessing quadrupole moments (such as X in PX_3 in P^{31} spectra) were unable to induce sharply defined multiplets due to spin relaxation effects.

Since these multiplets were shown to occur despite rapid molecular reorientation, and since they were not produced by interactions of equivalent nuclei, they are not caused by direct magnetic dipole-dipole interaction. Independence of field strength rules out a direct second-order interaction. However, dependence upon nuclear magnetic moments (4) and electronic structures of various molecules suggests a second process in which one nucleus induces a magnetic moment in the electron distribution of the molecule, the induced moment then interacting through space with the second nucleus.

Via this mode of interaction, the field at one nucleus should be proportional to the magnetic moment of the other, the energy of interaction being proportional to the product of the two moments. Since the multiplets persist during rapid molecular reorientation, the interaction must depend upon the relative orientation of the nuclear moments, being of the form $hJ_{12}I_{1/2}$ (J =coupling constant). Also, since the interactions of the electrons with applied magnetic fields and with thermal jostlings are small compared to the electronic energetics associated with the multiplet interaction, the coupling constant should be independent of field strength and temperature.

Since magnetization induced by magnetic nuclei can involve either electron orbital magnetic moments, electron spin magnetic moments, or both, second order perturbation theory has been used to show that spin effects are far more important than orbital motion effects in the coupling mechanism.

THEORY:

The theory used here is essentially that of Ramsey (5), which is also followed in other widely read references on coupling constants (6,7). The Hamiltonian, ignoring nuclear dipolar interactions, which average to zero for molecules in the liquid state, can be written

(1) $H = H_1 + H_2 + H_3$, where

(2) $H_1 = \sum_k \frac{1}{2mk} \left(\frac{\hbar}{i} \nabla_k + \frac{e}{c} \sum_N \chi_N \bar{I}_N \times \frac{r_{kN}}{r_{kN}^3} \right)^2 + V + H_{11} + H_{1s} + H_{ss}$.

The terms V , H_{11} , H_{1s} , and H_{ss} denote respectively interactions due to electrostatic, electron orbital-orbital, spin-orbital, and spin-spin interactions, none of which involve I_N , the nuclear spin angular momentum in terms of \hbar . The term $r_{kN} = r_K - r_N$, where r_K denotes the coordinate of the K th electron and in the coordinate for the N th nucleus.

(3) $H_2 = 2B\hbar \sum_{K,N} \chi_N [3(\bar{S}_K \cdot \bar{r}_{KN})(\bar{I}_N \cdot \bar{r}_{KN})r_{KN}^{-5} - (\bar{S}_K \cdot \bar{I}_N)r_{KN}^{-3}]$

This term represents the magnetic dipolar interactions between electrons in orbitals where $r_{KN} > 0$ and nuclear moments. S_K is the electron spin angular momentum in terms of \hbar and B is the Bohr magneton.

(4) $H_3 = \frac{16\pi B\hbar}{3} \sum_{K,N} \chi_N \delta(r_{KN}) \bar{S}_K \cdot \bar{I}_N$

H_3 is the Fermi contact term between electron spins in orbitals in which $r_{KN} = 0$ and nuclear magnetic moments. $\delta(r_{KN})$ is the Dirac δ function which picks out the value at $r_{KN} = 0$ in any integration over the coordinates of electron K .

The energy of the electron spin coupling of nuclei N and N' , denoted E_{NN}' , is obtained from consideration of the above terms (5-7) by considering only those terms which simultaneously involve I_N and $I_{N'}$. Thus:

(5) $E_{NN}' = hJ_{NN}' I_N \cdot I_{N'} + hI_N' \cdot J_{NN}' \cdot I_N$, where J_{NN}' is the coupling constant and J_{NN}' is dyadic (a symmetrical linear vector matrix) with trace zero. Since high-frequency molecular motions in the liquid state average the second term to zero, with both nuclei coupled to a fixed electric field, we obtain

(6) $E_{NN}' = hJ_{NN}' \cdot I_N \cdot I_{N'}$

For liquids undergoing rapid molecular reorientations, and for substances in which there is no strong electron spin-orbit coupling, all cross terms in the Hamiltonian vanish, leaving

(7) $J_{NN}' = J_{NN}'^{(1a)} + J_{NN}'^{(1b)} + J_{NN}'^{(2)} + J_{NN}'^{(3)}$

$J_{NN}'^{(1a)}$ and $J_{NN}'^{(1b)}$ represent nuclear spin coupling via electron orbital motion, arising from the expansion of H_1 and consideration of those terms involving I_N . $H_1^{(a)}$ is of second order in nuclear spins and $H_1^{(b)}$ of first order. $J_{NN}'^{(2)}$ represents magnetic dipolar interactions between electrons in orbitals with $r_{KN} > 0$ and nuclear spins,

while $J_{NN}^{(3)}$ is the contribution due to the Fermi contact term, involving J_{NN} interaction between electron spins in which $r_{KN} = 0$ and nuclear magnetic moments.

Thus, while calculations (5,6) have shown that $J_{H-H} \approx J_{NN}^{(3)}$, we must consider other terms in the case of J_{F-F} , since $J_{NN}^{(2)}$ is not negligible and $J_{NN}^{(1a)}$ and $J_{NN}^{(1b)}$ are sometimes of suitable magnitude to be considered.

McConnell et al. (6,9,12) and Karplus (11) have performed the theory in the area of fluorine-fluorine coupling constants. In examining $CF_2 = CF_2$, McConnell (6) observed that, due to electron exchange, the electron orbitals terms $J_{NN}^{(1a)}$ and $J_{NN}^{(1b)}$ contributed significantly to the coupling even though separated by several bonds. In this case, both one electron integrals--arising from magnetic interaction of nucleus N with an electron on nucleus N', which in turn interacts with nucleus N--and two electron integrals--arising from the perturbation induced by nucleus N upon a "local electron," which then interacts directly with an electron belonging to nucleus N', the latter electron then interacting with nucleus N' were considered (8). However, it is stated that even order-of-magnitude considerations for J which would include fluorine-fluorine π bonding, conjugation with the carbon π system and σ -bonding are impossible for $CF_2 = CF_2$ due to the unknown bond orders and the unknown degree of S-P hybridization on the fluorine atoms. Other work, however, (9, 12) concerning less highly fluorinated olefins has yielded theoretical coupling constants which compare favorably with experiment.

Karplus (11) has examined the high resolution F^{19} n.m.r. spectra of $CHF = CHF$ (cis and trans) by use of the valence bond theory. By utilizing nonp~~er~~fect pairing structures, with suitable approximations, and by neglecting all terms except the contact term, $J_{NN}^{(3)}$, the justification being that calculations had shown the other terms to be small, fairly good agreement was obtained between theoretical and experimental (9,12,13) results. Similar work (10) has also been performed upon deuterated fluorobenzenes.

The experimental data (9,12,13) show $J_{N-N}^{(trans)} > J_{N-N}^{(cis)}$, a situation predicted by both MO and VB theories. In the case of J_{F-F} , the contact term (11) explains the order of magnitude of the splitting, while with J_{H-F} , the contact term largely determines J_{H-F} , although other terms may be significant.

Recently Evans (14) has investigated the series $CF_2 = (FX)(X=Cl, H, CH_3)$, observing $J_{F-F}(trans) > J_{F-F}(cis)$. However, the results show that the approximation made by Karplus (11) is not completely valid, and that terms of the type used by McConnell (6) are important.

Although the original assignments by McConnell (6) of the various peaks observed to certain couplings was not unambiguous, recent work (15,16) on similar compounds using spin decoupling techniques have confirmed his original assignments.

Unexplained lines in the spectra of $\text{CF}_3\text{CCl} = \text{CFCl}$ and $\text{CF}_3\text{CCl} = \text{CF}_2$ (16) have been observed and are thought to be due to the hindered rotation of the CF_3 group. A group of four substituted gem-difluoroethanes (18) were also found to have extra lines in the spectrum due to hindered rotation. The structures of the compounds studied were determined by consideration of the coupling constants obtained.

The ABP system, $\text{F}_2\text{BrC}-\text{CFHCl}$ (17), was observed to possess $J_{\text{AP}} \approx J_{\text{BP}}$, indicating the populated forms of the molecule to be those in which the bromine was situated trans rather than gauche to the A and B fluorines.

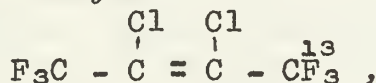
THROUGH-SPACE COUPLING:

Gutowsky and Saika (19) have reported the first case in which J_{AB} for fluorines on adjacent carbon atoms is \approx zero. For $(\text{CF}_3)_2\text{N}-\text{CF}_2\text{CF}_3$, Gutowsky has proposed that two or more contributions of equal magnitude and opposite sign were responsible for this anomalous coupling constant. Crapo and Sederholm (20) have explained similar behavior in $\text{CF}_3\text{CF}_2\text{CFICl}$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{COOH}$ by suggesting the presence of hindered rotation about the carbon-carbon bond, such that the coupling constant is approximately zero when the molecule is in the staggered configuration (lowest potential energy) and is non-zero otherwise.

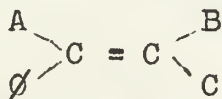
Petrakis and Sederholm (8) have recently published a large study of fluorocarbons containing perfluoroethyl and higher chains. A mechanism of through-space coupling based on empirical consideration has been proposed to account for $J_{\text{ac}} > J_{\text{ad}} > J_{\text{ab}} (J_{\text{ab}} \approx 0)$ in many cases.

This mechanism assumes 1) coupling through the bonds is negligible, in opposition to proton systems; 2) such coupling decreases rapidly as the number of intervening bonds increases; 3) in fluorine coupling the main contribution is directly through space; 4) 2.73 \AA is too great a distance for through-space coupling; and 5) 2.73 \AA is just outside the distance at which through-space coupling becomes important. The exceptions to this study (8,21) are generally explained by steric interaction.

This paper has been widely referred to as an explanation for unexpected coupling constants. Work performed by Roberts et al. (22) was sighted in the original paper as an example of the occurrence of through-space coupling in H-F systems. Tiers (23) has studied cis and trans



noticing J_{FF} to be larger in the cis position than the trans, opposed to the findings of McConnell (6) but consistent with Petrakis and Sederholm (8). Andreades (24) has found CF_3-CF_3 coupling to be greater in (A,B,C = CF_3 or F, such



that no one species is present alone) in the cis position, although F-F coupling was as expected (6).

The empirical nature of this mechanism is its main detractor. Several authors (24,25) have expressed doubt or caution as toward its acceptance, primarily due to the fact that it has been tested on only a limited number of compounds and has no theoretical background.

ABSOLUTE AND RELATIVE SIGNS OF COUPLING CONSTANTS:

Karplus (26) has theoretically predicted the presence of opposite signs for coupling constants, stating that " J_{HH} " is taken to be positive when the antiparallel nuclear spin orientation leads to a lower energy state than the parallel orientation." The experimental method used for determining the relative signs of the coupling constants has been that of the double resonance technique (27), the operation of which is described in the above reference. Two reviews on this subject have recently appeared (28,29), and the reader is referred to them for a greater knowledge of this technique.

Elleman, Manatt and Evans (14,30-32), in studying a large number of fluorosubstituted ethanes and ethylenes, have found that in cases in which there are several different types of couplings, these couplings generally do not all possess the same relative sign.

Tiers (33-35), assuming $J_{C^{13}-H}$ to be positive, has examined several C^{13} -fluorocarbons, determining J_{H-F} and $J_{C^{13}-C-F}$ to be positive and $J_{C^{13}-F}$ to be negative relative to $J_{C^{13}-H}$.

Baldeschwieler and co-workers (36) have examined the spectrum of the two isomers of N_2F_2 by use of the double resonance technique, and have determined that $N = N \begin{smallmatrix} \diagup F \\ \diagdown F \end{smallmatrix}$ is not the species present along with

$N = N \begin{smallmatrix} \diagup F \\ \diagdown F \end{smallmatrix}$, but rather that the cis-isomer is present.

Heffernan and White (37) have examined the AB_2X_2 spectrum of $P_3N_3F_2Cl_4$, in which both fluorines are attached to the A phosphorus. J_{AB} (phosphorus-fluorine attached to phosphorus) and J_{BX} were found to be of opposite sign from J_{AX} upon examination of the unsymmetrical fluorine multiplets at low fields.

Baldeschwieler and co-workers (38,39) have examined the $AA'XX'$ spectra of the three isomers of $C_2H_2F_2$, determining in every case that all H-F coupling constants were of the same sign in the liquid phase, while all proton-proton coupling constants were of opposite sign toward the fluorine-fluorine coupling constants in the gas phase.

Recently, it has been proposed (40) that it might be possible to determine the absolute sign of a coupling constant by subjecting the sample being studied to an electric field, E . This theory has proposed that if the coupling constant be negative, application of the electric field will increase the splitting, and if it be positive, decrease the splitting, the change in splitting being proportional to E^2 , the strength of the field.

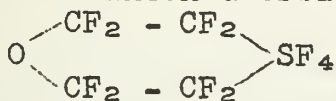
An application of this theory has recently been reported (41). An AB system, P-nitrotoluene, was studied under a strong electric field in the manner outlined. Application of the field decreased the ortho ring coupling constant, indicating its positive nature, while variation of the field caused a variation of the coupling constant ($\Delta J \propto E^2$) as proposed by theory.

Of particular interest to the inorganic chemist is the fact that if $J_{C^{13}-H}$ were chosen to be positive, the ortho ring constant is also positive. Thus, the assumptions by Tiers (33-35) and others that $J_{C^{13}-H}$ is positive is correct. This situation then fixes the sign of $J_{C^{13}-F}$ as negative, allowing the absolute signs of the various kinds of J_{F-F} to be determined readily from fluorocarbon systems, and these results then applied to inorganic systems.

APPLICATIONS IN INORGANIC CHEMISTRY:

A number of investigations (42-52) have been performed on the system SF_4AC , in A and C are trans to each other. A is either fluorine or a substituted group, whereas C is always a substituted group. The appearance of the spectrum for SF_5C depends upon R, the ratio of J_{AB}/S_{AB} , where A and B are the two types of fluorines. The spectrum varies from AB_4 when $S \approx J$ as in SF_5OF , in which a twenty-one line spectrum as predicted by McConnell (6) is obtained, to AX_4 when $S \gg J$ as in SF_5Cl , in which overlap of the spectrum causes difficulty in interpretation. These complex spectra may be understood only by consideration of off-diagonal elements in the Hamiltonian matrix (43, 53), and are due physically to second-order spin-spin interaction (44).

In the approximately sixty compounds studied, J_{AB} remained essentially constant ($J_{AB} = 149 \pm 6$ CPS) and seemingly independent of the nature of C. Thus, it is safe to assume that the geometrical positioning of these groups is not altered to a great extent by the various groups present. J_{AX} (X is a fluorine on the substituted group C) was always found to be near zero, indicating essentially no interaction between the apical fluorine and those fluorines contained in groups located trans to it. Use of S^{33} to determine changes in hybridization of the two types of sulfur-fluorine bonds in a manner similar to C^{13} studies is prohibitive because of the low natural abundance of S^{33} and its large spin (.75% and 5/2, respectively) (54) and the fact that Gutowsky's equation for $J_{C^{13}-H}$ (55) is not completely applicable to systems in which d-orbitals are used in the hybridization. The compound



This change in J is due to the fact that the C-S-C angle is now approximately 90° instead of 180° as is observed in octahedral systems. Thus, we have an A_2B_2 system, for which we would expect an entirely different coupling constant.

The spectrum of $(CF_3)_2CFS(O)OCH_2CH_3$ has been found (50) to be temperature dependent, thus indicating the presence of hindered rotation

in the molecule. At -20° ,
two separate multiplets
corresponding to
 J_{AX}

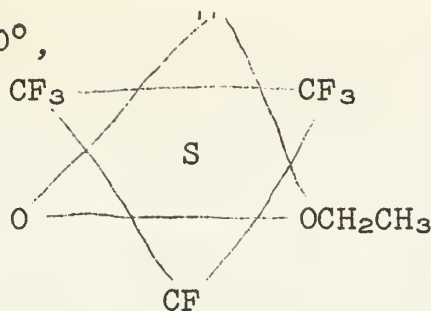


Fig. 1

and J_{BX} were obtained. Since $J_{AX} = J_{BX}$, this is an indication that the favored configuration at this temperature is trans rather than gauche.

Many of the AX and BX coupling constants obtained in these studies have been explained in terms of the through-space coupling mechanism proposed by Petrakis and Sederholm (8) or in spite of it. For example, J_{AX} and J_{BX} for SF_5OF have been reported as 0.0 and 17.4 CPS (48) and -0.6 and 18.2 (49) CPS. Harris and Packer (49) have explained the size of J_{B-X} in terms of the through-space coupling, since the B and X fluorines are separated by three bonds. The apparent lack of a J_{AX} coupling constant is explained in light of the trans nature of the substituents which prohibits the spin-spin coupling. Similarly, in SF_5OSO_2F (42), in which the B and X fluorines are separated by four bonds, the values of $J_{BX} = 7.2$ CPS and $J_{AX} = 0$ are explained in the same manner. (It is interesting to note that these coupling constants are the same order of magnitude as those which were observed in systems containing carbon and nitrogen bonds (8), thus lending additional possible support to such a mechanism.)

Boden et al. (51) have examined a series of alkyl substituted SF_6 compounds. Since $J_{HF} > J_{HH}$ for most of the cases encountered, the fluorine spectra were regarded as the AB_4 parts of more complex spectra. In all cases observed (SF_5X , where $X = \text{vinyl, isovinyl, chloroethyl, 2-chloro-n-propyl, 4-chloro-n-butyl}$), although there were no F^A-H splittings, there were F^B-H splittings observed over three and four bonds. Thus, the authors have regarded the presence of basal fluorine coupling only ($J_{F-CH_2} \approx 8\text{CPS}$) as evidence for a spatial mechanism for spin-spin F^B interaction. (Note that this is similar to what has been reported by Roberts (22).)

Rogers and Graham (52) have studied six compounds of the type ASF_4C , where A and C are usually perfluoroalkyl groups. The spectra of $(CF_3CF_2)_2SF_4$, $CF_3SF_4CF_2COOCH_3$, and $CF_3SF_4CF_2CF_3$ are normal (No CF_3-CF_2 splitting or H-F splitting), the one of $CF_3CF_2SF_5$ a little more complex, since there are 27 lines in the apical fluorine spectra, and the ones for $CF_3CF_2CF_2CF_2SF_4$ and $CF_3SF_4CF_2SF_4F$ are complex but reasonable.

The coupling constants obtained varied in no coherent manner with the number of bonds separating the interacting nuclei, and seemed to give some justification to the through-space coupling mechanism (8).

It is mentioned, however, that rotational averaging of trans and gauche F-C-C-F couplings of opposite sign ($J_{\text{gauche}} = -1/2 J_{\text{trans}}$) could lead to a coupling constant of zero for fluorines on adjacent carbons. It is also stated that the numbers obtained have little significance, since the effect of geometry on the through-bond couplings in octahedral molecules is unknown, as are the effects of rotational averaging.

Since $\text{CF}_2\text{-SF}_6$ coupling constants of $\approx 5\text{CPS}$ were obtained for the latter three compounds mentioned, Rogers and Graham have cast strong doubts upon the through-space hypothesis. They have also pointed out that Manatt and Elleman (32) obtained $J_{\text{trans}} = 18.6\text{ CPS}$ and $J_{\text{gauche}} = 16.2$ for $\text{CF}_2\text{Br - CBr}_2$, values which it is thought cannot be explained by through-space coupling. However, since the signs of both coupling constants in $\text{CF}_2\text{Br-CBr}_2$ are the same, the authors are rather puzzled as to what the situation is in compounds where $J_{\text{F-C-C-F}} \approx 0$. (It should be noted that Petrakis and Sederholm (8) studied two compounds similar to the one above, obtained non-zero coupling constants, and explained them in terms of steric hindrance which pushed the fluorines closer together so as to give $J_{\text{F-F}} > 0$.)

Several studies have recently appeared concerning $J_{\text{C13-F}}$ coupling constants. Harris (56,57) has shown that in a series of compounds CF_3X , as Z_X increases within a family, $J_{\text{C13-F}}$ increases by approximately 20 CPS per member, opposite to what has been observed for $J_{\text{C13-H}}$. As Z_X increases within a given row, $J_{\text{C13-F}}$ decreases by 8-12 cycles, again opposed to $J_{\text{C13-H}}$. However, Tiers (33) has shown $J_{\text{C13-F}}$ to be of opposite sign to $J_{\text{C13-H}}$, so that in both cases the two trends presumably have the same absolute sign. The variation of $J_{\text{C13-F}}$ among the various sulfur compounds listed shows that the effect of remote substituents is comparable in magnitude with the differences observed across the periodic table. Since differences in J for which X belongs to two different rows are twice that for X belonging to the same row, Harris has concluded that there is no simple comparison of $J_{\text{C13-F}}$ in $(\text{CF}_3)\text{X}$ with the electronegativity of substituent X .

TABLE I.

Comparison of $J_{C^{13}-F}$ for $(CF_3)X$

J					
CF_4	259.2	$(CF_3)_2NNO_2$	273.6	$(CF_3)_2PCl$	320.2
CF_3H	274.3	$(CF_3)_2PCl$	320.2	$(CF_3S)_2$	313.8
CCl_3F	336.5	$(CF_3)_2AsCl$	344	CF_2Br_2	357.0
$(CF_3S)_2$	313.8	$(CF_3)_2CCl_3$	282.5	CF_2Cl_2	324.3
$(CF_3Se)_2$	331.3	$(CF_3)_2NNO_2$	273.6	$CFBr_3$	371.7
$(CF_3)_2S$	309.4	CF_3SH	304.1	Values for the last two compounds indicate attachment of the ligand through the sulfur atom.	
$(CF_3S)_2$	313.8	CF_3SCSF	312.4		
$(CF_3S)_2Hg$	308.3	CF_3SNCO	309.3		

In an attempt to extend the work of Gutowsky and Juan (55), the following formulae for $J_{C^{13}-F}$ have been proposed.

$$(8) \quad J_{C^{13}-F}(CF_3X) = 2 \int_F + \int_X, \text{ where } \int_F = 86.4 \text{ CPS}$$

$$(9) \quad J_{C^{13}-F}(CF_2X_2) = \int_F + 2 \int_X + \Delta_X$$

$$(10) \quad J_{C^{13}-F}(CFX_3) = 3 \int_X + 3 \Delta_X$$

From other information not given here (57), the values for J_{CF_3X} were obtained. ($J_{C^{13}F_2Br} = 319.5$, $J_{C^{13}F_2Cl} = 298.5$) Upon utilizing the formulas, values of $\int_{Br} = 146.7$ and $\int_{Cl} = 125.7$ CPS and $\Delta_{Br} = -22.8$ and $\Delta_{Cl} = -13.5$ CPS are obtained. These results thus show that there are deviations from the behavior observed with $J_{C^{13}-H}$. Thus Harris has concluded that the s-character in the $C^{13}-F$ bond is probably not the dominating factor of determining $J_{C^{13}-F}$, as it is in $J_{C^{13}-H}$.

Harris has also observed some coupling constants in order to test the through-space hypothesis. His value of J_{F-F} for $(CF_3)_2Hg = 5.3$ CPS is far too large to be explained by through-space coupling if the system is linear as with $(CH_3)_2Hg$. Also, the values of J_{F-F} over five bonds ($J_{(CF_3S)_2} < J_{(CF_3O)_2}$ but $J_{(CF_3)AsSCF_3} > J_{(CF_3)_2PSCF_3}$) do not seem consistent with any other factor.

van der Kelen and Eeckhaut (58) have studied a series of fluorinated nitriles, acids, esters, and alcohols, determining

TABLE II.

	$J_{C^{13}-F}$	$J_{C^{13}-C-F}$		$J_{C^{13}-F}$	$J_{C^{13}-C-F}$		$J_{C^{13}-F}$	$J_{C^{13}-C-F}$
CH ₂ FCH ₂ OH	167 CPS	----	CHF ₂ CH ₂ OH	240.5	---	CF ₃ CH ₂ OH	279	---
CH ₂ FCOOH	181	21.8	CHF ₂ COOEt	243	28	CF ₃ COOH	282	43.6
CH ₂ FCN	172	25.3	CHF ₂ CN	243.5	40	CF ₃ CN	264	58

here that $J_{C^{13}-F}$ is only weakly influenced by the hybridization state of the carbon $-F$ (C^{12}) attached to the fluorinated methyl group.

Thus it would appear that factors other than the S-character in the $C^{13}-F$ bond govern the coupling constant $J_{C^{13}-F}$.

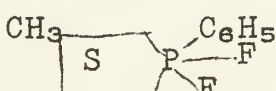
Recently, work has been reported on one of n.m.r.'s earliest anomalies, the equivalence of all fluorines in PF₅ (1). Mahler and Muetterties (59) have examined the AB₃X₃ system, CF₃PF₄. From the possibilities of 1) a small chemical shift between the equatorial and apical fluorines; 2) fast intermolecular exchange (discounted due to the simplicity of the spectrum); 3) intramolecular exchange, such as in IF₅, and 4) $J_{FF} \gg \delta$, which might be used to explain the magnetic equivalence, it was first reported that an abnormally small chemical shift (.07PPM) could be used to explain the spectrum. This chemical shift was observed over a wide range of temperatures, and it was for a time felt that the same situation must exist in PF₅. Although the small chemical shift could not be explained by intramolecular exchange, the small AB coupling constant (12 CPS) and identical J_{P-F_a} and $J_{P-F_b} = 1103$ CPS caused further studies to be undertaken, which resulted in a reinterpretation of the results.

Holmes and Gallagher (60) prepared PCl₄F, PCl₃F₂, PCl₂F₃, δ -PCl₄F, and δ PCl₃F₂, finding for all a doublet in the F¹⁹ n.m.r. spectrum. In the case of the latter two compounds, this is an indication of lack of ionization of the fluorines (definitely in the first, probably in the second) upon reaction. The authors were reluctant to assign structural formulae to the chlorofluorides, since they were under the influence of the preceding paper (59) and its assumption of an immeasurably small chemical shift for F_A and F_B in PF₅. However, it was obvious that they preferred the fluorine ligands in equatorial positions.

Muetterties et al. (61) have recently reported a large amount of data concerning the stereochemistry of substituted PF₅ compounds. IR and n.m.r. studies indicate that in the case of R₃PF₂, all R groups are in equatorial positions. The rather remarkable

TABLE III

J_{P-F} for a Series of Trisubstituted PF₅ Molecules

Comp.	J_{PF}	Comp.	J_{PF}
(CH ₃) ₃ PF ₂	545	(C ₆ H ₅) ₃ PF ₂	695
(C ₂ H ₅) ₃ PF ₂	575	(CF ₃) ₃ PF ₂	988
(n-C ₄ H ₉) ₃ PF ₂	585	CH ₃ -  -F	630

span of P-F coupling constants is explained by possible changes in hybridization at the phosphorus or variations in the P-F distance, bond distance and non S-character to the axial fluoride decreasing as J increases. It is also found that the P-F stretch in $(\text{CF}_3)_3\text{PF}_2$ is considerably higher than in other trisubstituted compounds, indicating a shorter bond distance.

Hyperfine structure in the F^{19} n.m.r. of disubstituted PF_5 molecules favors substitution in equatorial positions, while chemical shift data has ruled out a square pyramidal structure. Coupling constant and IR P-F stretch data have been interpreted so as to show the apical P-F bond distances to be longer than the equatorial, and so as to show the apical P-F bond distances to be longer in R_3PF_2 than in R_2PF_3 . The compound $(\text{CH}_2)_4\text{PF}_3$ was found to undergo an intramolecular exchange, with a barrier to exchange of ≈ 7 kcal/mole. The structure for Cl_2PF_3 and Br_2PF_3 , though not completely established, appears to be one in which both non-fluorine ligands are in apical positions, though at room temperature the chlorides and possibly the bromides undergo exchange.

Study of the monosubstituted PF_5 species has revealed only one type of fluoride (here Muetterties withdraws his earlier speculation concerning CF_3PF_4 and its small chemical shift (59)), thus making possible a tetragonal pyramidal structure with the substituted group in an apical position or trigonal bipyramidal structures with the substituted group in either an equatorial or apical position with the fluorines undergoing rapid intramolecular exchange. Chemical shift and coupling-constant data, however, favor equatorial substitution, with the exception of CF_3PF_4 which is thought to be substituted in an apical position. The analogy to PF_5 is used as the rationale for preferring the trigonal bipyramidal structure over the square pyramidal one.

Hoffman, Holder, and Jolly (62) have determined the structure of liquid SbF_5 by F^{19} n.m.r., in conjunction with electrostatic and orbital considerations. At -10° 3 peaks of ratio 1:2:2 were obtained, which at higher temperatures collapsed into one broad peak at $\approx 80^\circ$. Peak one was unresolved, peak two was split into seven detectable signals, and peak three into three signals. It was assumed that due to its large quadrupole moment ($\text{Sb}^{121} = 5/2$, $\text{Sb}^{123} = 7/2$) (54), antimony did not split the fluorine resonances; thus the fluorine spectrum was determined on the basis of the three types of fluorines splitting one another. The structure proposed is a polymeric one.

The peak due to A is split into a triplet by B ($J_{AB} = 70$ CPS), but further splitting by C broadens the peak so as to make determination of the individual resonances impossible. B is split into a triplet by C ($J_{BC} = 135$ CPS), and then further split by A into a seven line spectrum of intensity 1:2:3:4:3:2:1, caused by the overlapping of the splittings (since $J_{BC} \approx 2J_{AA}$). C is split into

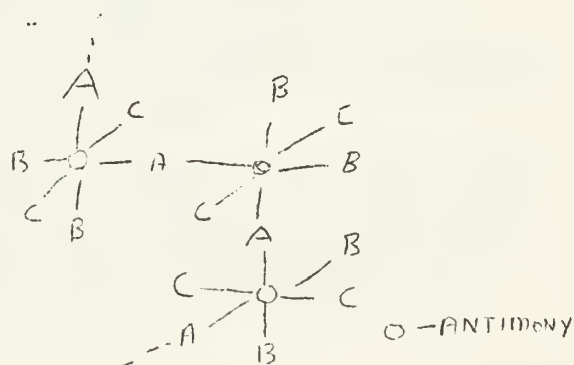


Fig. 2

a triplet by B, but no further splitting by A is observed. The collapse of the spectrum at higher temperatures is reportedly due to exchange, t_{lifetime} for any fluorine at 80° being $< 10^{-4}$ sec.

Seyferth, Wada, and Maciel (63) have begun a preliminary study of compounds of the form $\text{CF}_2 = \text{CFR}$, where R is an inorganic group.

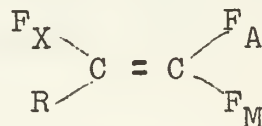


TABLE IV

R	$ J_{\text{AM}} _{\text{gem}}$	$ J_{\text{AX}} _{\text{cis}}$	$ J_{\text{MX}} _{\text{trans}}$
(OEt) ₃ Si	59.3 CPS	24.9	117.4
Et ₃ Si	70.5	26.5	115.1
Et ₃ Sn	78.8	31.9	115.5
Et ₃ Ge	80.7	33.7	113.7

Since J/δ was found to be small, the system was considered as an AMX system. Three quartets were obtained, as would be expected when second order interaction is present (6,9). Although no attempt was made to explain the magnitudes of the coupling constants as a function of R, it is easily seen that $|J_{\text{MX}}|_{\text{trans}} > |J_{\text{AX}}|_{\text{cis}}$, as predicted by McConnell and Karplus (6,9,11).

Muetterties and Phillips (64) have studied the exchange properties of a series of halogen fluorides. It was found that the 30 Mc spectrum of ClF_3 changed from a doublet and a triplet (with some smaller second order splitting of the peaks) at -40° to a broad line at 60° , whose position was approximately midway between the two original peaks. By obtaining lifetimes for the fluorines at -15° and 60° , an Eact of 4.8 kcal/mole was obtained.

The melting point of BrF_3 (8.8°) did not permit cooling to low enough temperatures for observation of multiplet splitting. Since only one peak was observable at room temperature, the fact for fluorine exchange was considered to be less in this case than in the case of ClF_3 .

Identical analyses were performed on IF_5 and BrF_5 . J_{AB} for IF_5 was measured as 81 CPS at 115° , the spectrum being uninterpretable at 175° . From measured lifetimes at 115° and 195° , an Eact of 13 kcal/mole was estimated for IF_5 . The lack of broadening of the BrF_5 spectrum at $\approx 180^\circ$ was an indication that no exchange was taking place, and that the system possesses a very high Eact.

Thus, the rate of exchange was found to be $\text{BrF}_3 > \text{ClF}_3 > \text{IF}_5 > \text{BrF}_5$. Ionization of the halogen fluorides in a manner similar to that proposed by the "solvent-system concept" does not correctly explain the order of exchange $\text{ClF}_3 > \text{IF}_5$, in fact predicting the opposite to be true. Dissociation of the halogen fluorides does not explain the

behavior of ClF_3 , giving a slower rate of dissociation at 454° than 223°K , where n.m.r. line studies give the opposite impression. However, dimerization through use of unfilled low-lying d-orbitals yields an order of stability $\text{BrF}_3 > \text{ClF}_3 > \text{IF}_5 > \text{BrF}_5$, exactly the same order as was determined for fluorine exchange, and the order we would intuitively expect, since the most stable dimer should undergo the reaction leading to dimerization with the fastest rate. Thus, on this basis, dimerization has been proposed as the mechanism for the observed fluorine exchange.

CONCLUSION:

The field of inorganic applications to fluorine-fluorine couplings has been little exploited and is not well understood. The field of fluorine-fluorine coupling constants in general awaits more theoretical work, in order to remove some of the empirical nature from it. The establishment of absolute signs for both $J_{\text{C}^{13}\text{-H}}$ and $J_{\text{C}^{13}\text{-F}}$ should spur interest in this growing field.

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THE BLOCH EQUATIONS AND THEIR USE IN INORGANIC CHEMISTRY

T. F. Bolles

August 1, 1963

INTRODUCTION

The description of the macroscopic nuclear polarization $M(t)$ of an assembly of nuclei under the influence of an external field $H(t)$ as a function of time gives rise to the Bloch equations. While the resulting "phenomenological equations" are not valid in all circumstances, in many cases they can qualitatively or even quantitatively describe the shape and magnitude of the observed nmr. signals. Modification of the Bloch equations also leads to the description of many systems.

The Bloch equations were first derived on a classical basis by Bloch (1) in 1945 to explain the observations of the nuclear magnetic resonance phenomenon by Bloch, Hansen and Packard at Stanford and by Purcell, Torrey and Pound at Harvard in that same year. In 1953, Bloch and Wangsness (2) developed this theory on a quantum-mechanical basis, which was later modified by Bloch (3) to include chemical shift effects. Since Bloch's original paper, many diversified treatments of the Bloch equations have been done to describe phenomena dependent on sweep rate, spin echo effects, free induction decay, and other time dependent effects (4).

THEORY

In the nuclear magnetic resonance experiment, a change in orientation of the macroscopic moment of an assembly of nuclei in a variable magnetic field causes observable voltages in a detector. The problem is to describe this nuclear polarization as a function of time and solve these equations, consequently giving a description of the observed signals. This will be done following Bloch's classical description of the macroscopic polarization.

The variable magnetic field is composed of two components: a strong static field, H_0 , produced either by an electromagnet or a permanent magnet, and at right angles to H_0 , a relatively weak radio-frequency field of amplitude $2H_1$ and circular frequency ω . The variation of the nuclear polarization vector $M(t)$ as a function of time in the total external magnetic field $H = H_0 + H_1$ is:

$$(1) \quad dM/dt = \gamma(M \times H)$$

where γ is the magnetogyric ratio of the nuclei involved. If the z-direction is that of the static R-F field, the total external field vector H has the components:

$$(2) \quad H_x = 2H_1 \cos \omega t ; \quad H_y = 0 ; \quad H_z = H_0 \quad .$$

We shall assume that the circular frequency ω of the R-F field is in the neighborhood of the resonance frequency $\omega_0 = \gamma H_0$ of the nuclei. It can then be shown (5) that the oscillating field in the x-direction can be effectively replaced by a field

$$(3) \quad H_x = H_1 \cos \omega t ; \quad H_y = \mp H_1 \sin \omega t$$

rotating about the z-direction. The sign of H_y is negative or positive depending upon whether γ is positive or negative. Using equations (2) and (3), the steady state solution of equation (1) now gives:

$$(4) \quad M_x = \frac{M \cos \omega t}{(1 + \delta^2)^{1/2}} ; \quad M_y = \frac{\mp M \sin \omega t}{(1 + \delta^2)^{1/2}} ; \quad M_z = \frac{M(\delta)}{(1 + \delta^2)^{1/2}}$$

where $\delta = \frac{(H_0 - H^*)}{H_1}$ and H^* is the resonance field at frequency ω , i.e., $H^* = \omega / |\gamma|$. It also can be shown that these solutions (4) are valid for $|d\delta/dt| \ll \gamma H_1$. (That is, if the variation of the field is slow with respect to the resonance width (6).)

If we note that $1/\tan\theta = \frac{H_0 - H^*}{H_1} = \delta$, then these equations predict that as $(H_0 - H^*)$ becomes small compared to the magnitude of H_1 , the direction of the polarization turns perpendicular to the z direction, then finally points in a direction opposite to H_0 for $(H^* - H_0) \ll H_1$. This "flipping" of the nuclear magnetization vector would be observed by the subsequent induction of an electric current in a detector.

Thus far, we have assumed that (1) the change in orientation of each nucleus is solely due to the presence of external fields and (2) the external fields are homogeneous throughout. Since (2) can be justified with sufficient experimental perfection, the main concern is with the first assumption. To arrive at modifications of equations (4) we need to investigate the changes in the polarization, $M(t)$, due to thermal agitation and internuclear action. The essential difference between thermal perturbations and internuclear interactions is that only thermal interactions can change the energy of the total spin system. Since the dominant portion of the total spin energy is due to the strong field, H_0 , in the z-direction, any significant change in the total energy of the spin system must result from a change in the z-component of the polarization. The equilibrium value which M_z will approach under the influence of thermal perturbations is:

$$(5) \quad M_0 = \chi H_0$$

where χ is the nuclear paramagnetic susceptibility. If at any time M_z is not equal to M_0 , Bloch assumed that the approach to equilibrium will be exponential with a characteristic "longitudinal" relaxation time, T_1 . Thus the change in M_z due to thermal perturbations is represented by:

$$(6) \quad \dot{M}_z = \frac{(M_z - M_0)}{T_1} .$$

The effect of internuclear moments is so small that their influence upon \dot{M}_z is negligible. However, they are of prime importance in the changes of the other two much smaller components of the polarization, M_x and M_y . Internuclear processes (as well as any other mechanisms such as inhomogeneities in H_0 or paramagnetic ions) which change M_x and M_y can be described by an "effective irregularity" of the z -field of order H' . The time which it takes for M_x and M_y to be appreciably affected is characterized by a "transversal" relaxation time, T_2 :

$$(7) \quad T_2 = 1/|\gamma|H'$$

Again, the change of the transversal components, M_x and M_y , are assumed to be exponential in character:

$$(8) \quad \begin{aligned} \dot{M}_x &= -M_x/T_2 \\ \dot{M}_y &= -M_y/T_2 \end{aligned}$$

The following differential equations are then obtained for the three components of the total polarization:

$$(9) \quad \begin{aligned} \dot{M}_x - \gamma(M_y H_z - M_z H_y) + M_x/T_2 &= 0 \\ \dot{M}_y - \gamma(M_z H_x - M_x H_z) + M_y/T_2 &= 0 \\ \dot{M}_z - \gamma(M_x H_y - M_y H_x) + (M_z - M_0)/T_1 &= 0 \end{aligned}$$

where, from (2) and (3)

$$(10) \quad H_x = H_1 \cos \omega t \quad ; \quad H_y = \mp H_1 \sin \omega t \quad ; \quad H_z = H_0$$

These equations are known as the classical Bloch equations.

In order to solve equations (9), it is easier to introduce the rotating axis system with angular velocity $-\omega$ about the z -axis and the components of the total polarization represented by u and v (u is parallel and v is perpendicular to the direction of H_1). The Bloch equations then are:

$$(11) \quad \begin{aligned} du/dt + u/T_2 + (\omega_0 - \omega)v &= 0 \\ dv/dt + v/T_2 - (\omega_0 - \omega)u + \gamma H_1 M_z &= 0 \\ dM_z/dt + (M_z - M_0)/T_1 - \gamma H_1 v &= 0 \end{aligned}$$

which have solutions:

$$(12) \quad \begin{aligned} u &= M_0 \left(\frac{\gamma H_1 T_2^2 (\omega_0 - \omega)}{(1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2)} \right) \\ v &= -M_0 \left(\frac{|\gamma| H_1 T_2}{(1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2)} \right) \\ M_z &= M_0 \left(\frac{1 + T_2^2 (\omega_0 - \omega)^2}{(1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2)} \right) \end{aligned}$$

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The importance of writing the Bloch equations in the rotating axis system is obvious when one remembers that the detectors used in the n.m.r. experiment observe the absorption, v , or the dispersion, u , component of the polarization. In most cases the absorption component, v , is observed. Therefore, the current induced in the detector is directly related to v . This relation is:

$$(13) \text{ Signal}_v \propto \left(\frac{\omega \chi_0 H_0 \gamma H_1 T_2}{(1 + T_2^2(\omega_0 - \omega)^2 + (\gamma H_1)^2 T_1 T_2)} \right) .$$

If $(\gamma H_1)^2 T_2 T_1 = 1$, the peak voltage is:

$$(14) V_{\max} \propto \omega_0 \chi_0 H_0 (T_2/T_1)^{1/2}$$

or, since $\chi_0 = \frac{(I+1)N\mu^2}{3IkT}$

$$(15) V_{\max} \propto \left(\frac{N(I+1)\mu^2}{IT} \right) (\omega_0 H_0 (T_2/T_1)^{1/2} .$$

where I is the nuclear spin, μ is the maximum component of the nuclear magnetic moment, N is the number of nuclei per unit volume and k is the Boltzmann factor.

Integrating equation (13) gives the area of the absorption signal:

$$(16) A_a \propto \frac{\chi_0 H_1}{(1 + \gamma^2 H_1^2 T_1 T_2)^{1/2}}$$

and the corresponding peak height is:

$$(17) S_{a(\max)} \propto \frac{\chi_0 H_1 T_2}{(1 + \gamma^2 H_1^2 T_1 T_2)} .$$

It should be emphasized that the case of "slow passage" has been assumed in these latter calculations, a condition which is usually satisfied. Other limitations of the Bloch equations for more complicated systems have been summarized (2,3).

APPLICATIONS

Measurement of Relaxation Times

One of the most important applications of the Bloch equations is in the evaluation of the relaxation times, T_1 and T_2 . There are two general techniques employed to measure relaxation times: continuous-excitation methods and pulse methods.

A. Continuous-excitation Methods

1. Progressive Saturation Method. (7,8)

Since the signal emplitude (Eq. 17) is dependent upon the "saturation factor," $(1 + \gamma^2 H_1^2 T_1 T_2)^{-1}$, when H_1 is progressively increased the variation of the signal amplitude is directly

proportional to H_1 . T_1 can then be evaluated from the value of H_1 if T_2 is known. However, since the proportionality factor in equation (17) must be known, this method is best used for comparison techniques.

2. Reversal-of-polarization Method. (9)

Under conditions of adiabatic rapid passage (ie, $\frac{dH_0}{dt} \ll |\gamma| H_1^2$), the relatively large radio-frequency field, H_1 , completely reverses the macroscopic nuclear magnetization vector, M . If H_0 is symmetrically modulated by a sinusoidal sweep, and if the time spent in resonance is short compared with T_1 , the amplitude of the signal on the return trace to equilibrium is proportional to the value M_1 of the magnetization at every passage. M_1 is given by:

$$(18) \quad M_1 = M_0 \frac{1 - e^{-t/T_1}}{1 + e^{-t/T_1}}$$

where $2t$ is the period of the sweep. Thus, if observations are made at different values of the sweep-time, t , T_1 can be determined.

Using this technique, T_1 has been measured for protons in H_2O - D_2O mixtures (10). The results showed a strong dependence upon the hydrogen concentration, supporting the dipole interaction mechanism for spin-lattice relaxation (7). This method has also been employed to support Bloch's hypothesis that paramagnetic ions in solution may act as catalysts in decreasing the spin-lattice relaxation time. This was done by measuring the effect of the first row transition metal ions upon aqueous proton relaxation times (11).

B. Pulse Methods

Along with the description of the n.m.r. experiment, Bloch also predicted the effect of the replacement of H_1 with a strong, short r-f pulse. This pulse turns the macroscopic magnetic moment from its equilibrium value. Thus, after the driving pulse has been removed, a transient nuclear induction signal is immediately observed as the magnetic moment precesses freely in the static field.

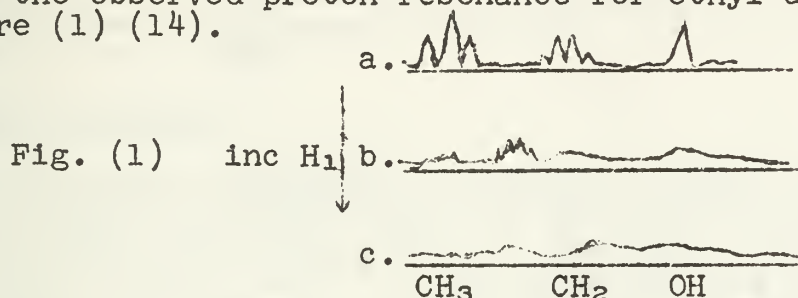
This theory has been applied to the effect of 90° pulses (12,13). It is found that when two 90° pulses are applied at times 0 and τ , an echo appears at time 2τ of amplitude:

$$(19) \quad A_{\text{echo}} \propto \exp\left[-\frac{2\tau}{T_2} - K \frac{(2\tau)^3}{3}\right] \text{ where } K \text{ is proportional to the self-diffusion constant of the sample. This constant can be eliminated by use of a } 90^\circ \text{ pulse followed by two } 180^\circ \text{ pulses at time } \tau, \text{ and } 2\tau, \text{ which will produce an echo at time } 4\tau \text{ (13).}$$

Modifications of this method have been devised, including a method to evaluate T_1 by using three 90° pulses (13). Pulse Methods have the advantage that the effects of saturation produced by H_1 are removed at the time of observation. In general, the pulse methods are far superior to the continuous excitation methods for the measurement of relaxation times.

Saturation Effects

Examination of equation (16) and (17) show that the area and peak height of the observed absorption signal are dependent upon the factors $(1 + \gamma^2 H_1^2 T_1 T_2)^{-1/2}$ and $(1 + \gamma^2 H_1^2 T_1 T_2)^{-1}$ respectively. The latter expression is commonly called the saturation factor. This expression shows that the degree of saturation depends upon the magnetogyric ratio of the nuclei involved, the relaxation times, and the magnitude of the radio-frequency H_1 . The effect of the strength of H_1 upon the observed proton resonance for ethyl alcohol is shown in figure (1) (14).



As expected, both the magnitude and area of the signal decrease as the strength of H_1 increases. The quartet appearing in (b) is due to a double-quantum transition expected from a quantum-mechanical analysis. Since the OH proton is in rapid exchange, no higher order quantum resonances appear between the OH and CH_2 resonance lines.

Saturation produces additional distortion in the n.m.r. signals (15). It is found that the reduction in signal height is greatest for the maximum value of the resonance line. This produces a "saturation broadening" of the resonance signal. In addition, different lines in a spectrum may have different relaxation times, and so be non-uniformly affected by saturation.

In general, saturation should be avoided for n.m.r. work. This may be done by using a small radio-frequency field, H_1 , or by decreasing the relaxation time of the nuclei being investigated (e.g., through "paramagnetic catalysts").

The Modification of the Bloch Equations to Include the Chemical Shift, and Analysis of Spin-spin Splitting.

Gutowsky, McCall and Slichter first modified the Bloch equations to describe phosphorus-fluorine spin-spin splitting effects by including an additional term for the chemical shift (16). The modified Bloch equations are:

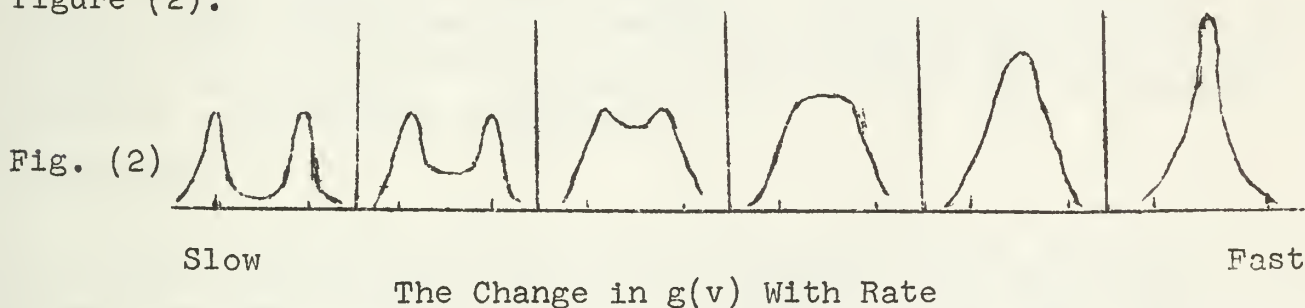
$$\begin{aligned}
 du/dt + (\Delta w + \frac{1}{2} w) v &= -u/T_2 \\
 (20) \quad dv/dt - (\Delta w + \frac{1}{2} w) u &= -v/T_2 - w_1 M_z \\
 dM_z/dt - w_1 v &= -(M_z - M_0)/T_1
 \end{aligned}$$

where $w_1 = \gamma H_1$, $\Delta w = \gamma H_0 - w$, and $\delta w/2$ represents the local field of phosphorus which causes the fine structure in the fluorine resonance. There are three more equations in which $\delta w/2$ is replaced with $-\delta w/2$ representing the other spin orientation of phosphorus. The solution of these equations shows a dependence upon the mean life, τ , of phosphorus in a given spin state. If τ is considered large, the solutions predict two resonance peaks of total splitting δw . If τ is small, a single line results showing a time averaging of the phosphorus spin. This demonstrates why nuclei with short relaxation times produce no spin-spin splitting, and also suggests the double resonance experiment.

Chemical Exchange

The method developed by Gutowsky, McCall and Slichter has proved to be of paramount importance in the study of rate processes with n.m.r. This is obvious from the dependence of the chemical shift (described above) upon τ , the lifetime of a chemical spin state, which also is related to the lifetime of chemical species in equilibrium.

The solution of the modified Bloch equations has been done for fast (17), slow (18), and intermediate (19,20) rates of exchange. The resulting change of the shape function, $g(v)$, for increasing rate of exchange between two sites with equal populations is shown in figure (2).



From the experimental signal shape, it is possible to determine the lifetime required for exchange. Considering two species in slow exchange (if the natural line width is small for both species compared to their separation), the rate can be determined from the broadening of the individual signals. In the intermediate region, the rate may be determined through a comparison of calculated spectra for various rates (21) with the experimental spectra, or by comparing the separation of the two maxima with the separation under conditions of slow exchange. For fast rates of exchange, the rate (or lower limit of the rate) is obtained from the width of the single resonance line.

This theory for fast exchange has been applied to the exchange of NH_3 with $\text{Ni}(\text{NH}_3)_6^{++}$ in aqueous and anhydrous ammonia solutions (22). Assuming the predominant species is $\text{Ni}(\text{NH}_3)_6^{++}$ in the range of $[\text{NH}_3]$ used ($7-14 \text{ M}$), the rate constant for a particular NH_3 exchange is about $6 \times 10^{-4} \text{ sec}^{-1}$ @ 30°C for both systems. Using the same technique, the limits for the exchange of water with hydrated Mn^{++} , Fe^{++} , Co^{++} , Ni^{++} and Cu^{++} using O^{17} resonance has been reported (23).

The rate of proton transfer between benzoic acid and methanol has been measured from a broadening of the methanol OH line (24). At -80° , the carbonyl hydrogen is observed. At higher temperatures, the spectra follow the trend in figure (2) until a single resonance is observed.

The lower limits for the rates of electron transfer between diamagnetic and paramagnetic species can also be measured using this analysis (25,26). In addition, n.m.r. can be applied to problems of internal rotation and molecular rearrangements.

Quantitative Analysis

Since the intensity of a n.m.r. line is proportional to the number of resonating nuclei present, the concentration of the resonating species can be determined from peak intensity measurements. Since the dispersion signal depends less critically on the strength of the H_1 field, the u component of the nuclear polarization is usually observed. The area of the dispersion signal is independent of T_1 and T_2 :

$$(21) \quad A_{u(\text{partial})} \propto \chi_{OH_1}$$

where A_u is integrated as far as the turning value. The proportionality factor can be determined from the analysis of standard solutions.

The n.m.r. method has been employed to determine the moisture content in agricultural and other natural products ranging from a few to 100 per cent. The precision of moisture analysis is of the order $\pm 0.1\%$ or better (27). At present, however, the area of quantitative analysis is relatively undeveloped.

CONCLUSION

Since the Bloch equations were first presented, many interesting and varied applications have been developed. Only the classical approach has been presented here. It should be noted that these solutions are the same as those developed through a quantum-mechanical derivation.

The limitations to the "phenomenological equations" (11) are:

1. $I = 1/2$; No restrictions.
2. $I = 1$; $H_0 \mu \ll kT$
3. $I > 1$ and negligible quadrupole-relaxation: $H_0 \mu \ll kT$
4. $I > 1$ and appreciable quadrupole-relaxation:

$$H_0 \mu \ll kT \quad \text{and} \quad T_1 = T_2.$$

Nevertheless, the phenomenological equations, because of their simplicity, have much empirical usefulness.

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INORGANIC SEMINAR ABSTRACTS

1963-64

FALL AND SPRING

Department of Chemistry and Chemical Engineering

University of Illinois

ASPECTS OF ALKYLHALOGENOBORANE CHEMISTRY

John H. Bright

September 17, 1963

The alkylhalogenoborane chemistry to be discussed will include some recent work concerning a method of preparation, relative boron-halogen pi-bonding, exchange reactions, and alkyl group isomerization.

Preparation from Trialkylboranes and Boron Trihalides

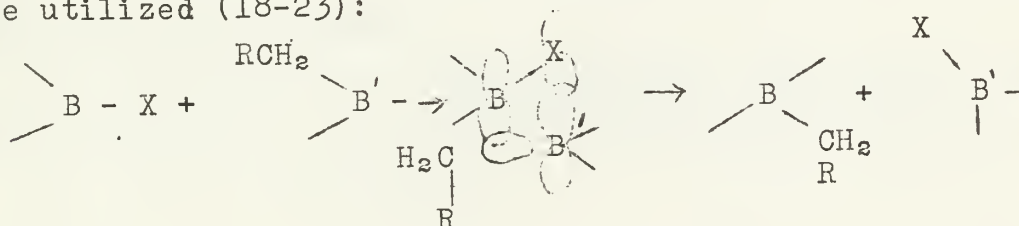
A number of preparations of alkylhalogenoboranes may be found in the literature (1,2). However, the reaction of trialkylboranes and boron trihalides provides a method for preparing either or both the alkyl dihalogenoboranes, RBX_2 , and dialkylhalogenoboranes, R_2BX , of fluorine, chlorine, and bromine (3-9). The reaction conditions vary depending upon the reactants, but temperatures of 130° and above are employed. The room temperature reaction of trialkylboranes and boron trihalides in the presence of a boron-hydrogen catalyst has been reported (10).

Pi-Bonding

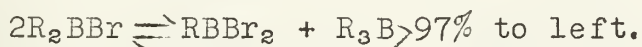
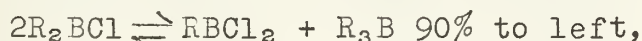
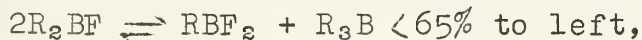
The relative pi-bonding in boron trihalides has been demonstrated by a number of properties including bond distances (11), Lewis acidities (12), force constants (13), and nuclear magnetic resonance spectroscopy (NMR) (14-17). The $p\pi-p\pi$ bonding decreases in the following order: $BF_3 > BCl_3 > BBr_3$. A similar order of decreasing pi-bonding has been demonstrated for the alkylhalogenoboranes employing alkyl alpha-proton NMR: $R_2BF_2 > R_2BCl_2 > R_2BBR_2$ and $R_2BF > R_2BCl > R_2BBr$. The relative methoxy-boron pi-bonding has been obtained by the application of methoxy-proton NMR. The following decreasing order of methoxy-pi-bonding is found: $RB(OMe)Br > RB(OMe)Cl > R_2B(OMe) > RB(OMe)_2 \sim B(OMe)_3$.

Exchange Reactions

Alkyl-halogen exchange occurs in the preparative reactions discussed above. A four-membered, bridged-dimer intermediate is hypothesized wherein boron p_z orbitals are utilized (18-23):

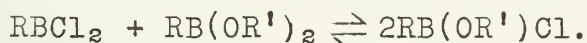
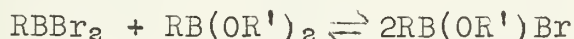


Certain redistribution reactions are observed for the alkylhalogenoboranes, and a similar bridged-dimer intermediate is proposed. For R_2BX compounds careful distillation at atmospheric pressure yields the products RBX_2 and R_3B for the chloro (6) and fluoro (21) compounds, but R_2BBR is stable with respect to redistribution to 170° (9). Approximate equilibria have been obtained for these reactions at 145° :

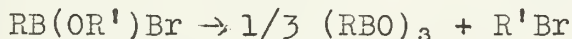


A marked contrast in redistribution behavior is observed for the RBX_2 compounds. The alkylidichloro (24) and difluoroboranes (25) are resistant to redistribution at temperatures to 180° , but the $RBBR_2$ compounds give R_2BBR and BBR_3 at temperatures as low as 95° (9).

Halogen-halogen exchange in boron trihalides (17,20,26,27) and alkylhalogenoboranes (23,28) have been observed. Also, evidence for alkoxy-alkoxy exchange has appeared (29-33). A preliminary study of halogen-alkoxy exchange has been carried out with respect to the following reactions:



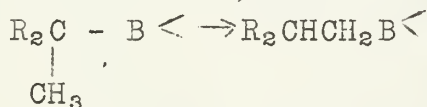
These reactions proceed at room temperature to equilibrium (about 90% to the right) in less than one-half hour. In the $RB(OR')Br$ cases, a further reaction takes place. Slow elimination of alkyl bromide ($R'Br$) is observed at room temperature. After five days 95% decomposition occurs. Rapid elimination is the case on attempts to distill a mixture containing the compound:



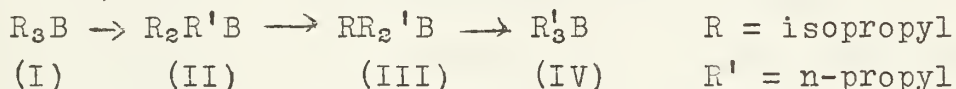
The $RB(OR')Cl$ compounds survive at room temperature on storage for several weeks.

Alkyl Group Isomerization

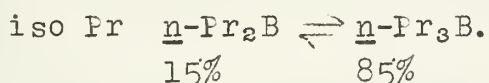
The isomerization of alpha-branched alkyl groups bonded to boron to primary alkyl groups has been observed for trialkylboranes (34), but little attention has been given to



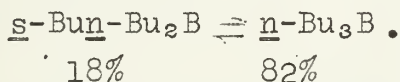
whether the reaction is reversible. "Reverse" isomerization has been demonstrated, and the equilibria approximately determined for the n-propyl/isopropyl and s-butyl/n-butyl trialkylborane systems (35). Temperatures in the range of 130-200° are required to bring about convenient rates. The isomerization of triisopropylborane has been shown to proceed through the unsymmetrical compounds (II) and (III) using gas-liquid chromatographic analysis (GLC):



Further, practically all of the trialkylborane exists as species (III) and (IV). At 145° the following equilibrium is found:



For the s-butyl/n-butyl case at 191° and at equilibrium 6% of the alkyl groups are found to be s-butyl. By analogy with the propyl system the following is proposed:



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THE CORPHYRINS, BIOCHEMICAL COORDINATION COMPOUNDS

L. J. Boucher

October 1, 1963

INTRODUCTION

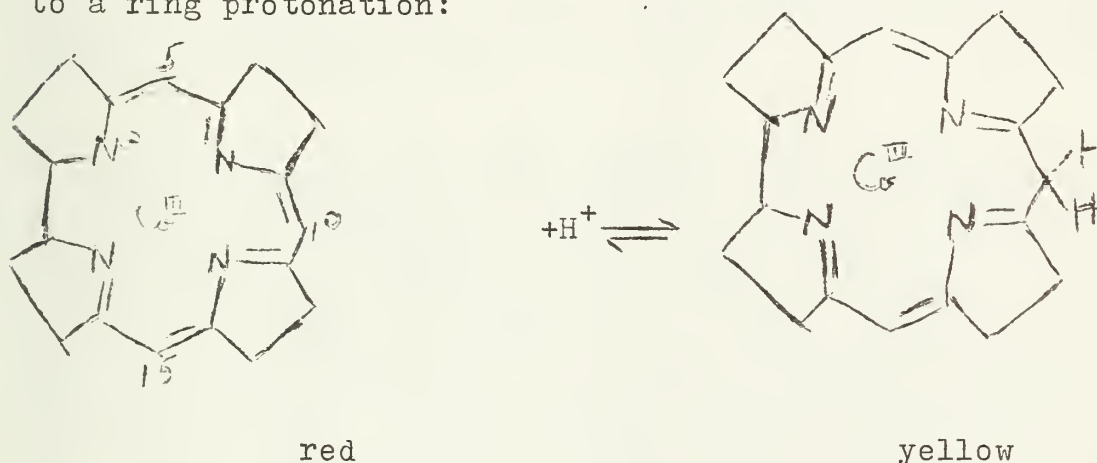
Vitamin B₁₂, the active substance used in the treatment of pernicious anemia, was first isolated in 1948 (1,2). It contains a cobalt(III) atom (3) bound to a planar tetrapyrrolic ring system, the corrin ring. A nucleotide base 5,6-dimethylbenzimidazole, and a CN⁻ fill the two remaining coordination positions above and below the plane. X-ray crystallographic analysis (4) has confirmed this structure. Compounds that possess the cobalt-corrin ring system are designated Corphyrins. A wide variety of B₁₂-like Corphyrins have been isolated and characterized. These differ from the original vitamin by replacement of the base in the nucleotide and by replacement of the CN⁻ by other simple ligands. There are also two reduced forms of the vitamin, i.e., B₁₂⁻, Co(II) (5), and B₁₂²⁻, Co(I) (6). In 1958 a new type of Corphyrin, Coenzyme B₁₂, was discovered (7). In it the CN⁻ is replaced by an adenosine nucleoside which is attached to the cobalt atom through a ribose carbon atom. This has been confirmed by x-rays (8). It can best be described as a cobalt(III) complex with a coordinated carbanion (9). Coenzyme B₁₂ which is believed to be the metabolically active form of the vitamin is the only naturally occurring compound with a cobalt-carbon bond. Several other forms of the coenzyme having different nucleotide bases have been isolated. Further, a series of corphyrins with carbanion ligands have been synthesized (10).

ABSORPTION SPECTRA (11)

The Corphyrins are highly colored and exist in two forms, red and yellow. In general their spectra are very complex with a number of clearly distinguishable bands of high intensity ($\epsilon_{\text{max}} \approx 10^4$). Red Corphyrin spectra have some striking similarities to that of the cobalt-porphyrin. Since the two ring systems are, to a first approximation, restricted to a plane, a similarity in the number and types of electronic transitions for the absorption spectra is to be expected. As the number of conjugated double bonds is less in Vitamin B₁₂ than in a porphyrin the band positions of B₁₂ are at shorter wavelength. The band system of the cobalt-porphyrin has one very strong band, the Soret or χ band at 411 m μ and two weaker bands at 529 and 560 m μ , the β and α bands (12). The spectrum of vitamin B₁₂ shows one strong band at 361 m μ and two weaker bands at 520 and 550 m μ ; these have been assigned as χ , β , α bands respectively. When the CN⁻ in the vitamin is replaced by other ligands there is a general shift to longer wavelength of the χ band as the σ donor and π acceptor

capacity of the ligand increases. The ligand series in the Corphyrins, where the electronic transitions originate in the organic chromophore, is the reverse of that observed for d-d transitions, i.e., the spectrochemical series. The intense bands in the spectra of the Corphyrins below 300 m μ are assigned to nucleotide base transitions. Replacement of the base in the nucleotide does not affect the γ , ϵ or α bands.

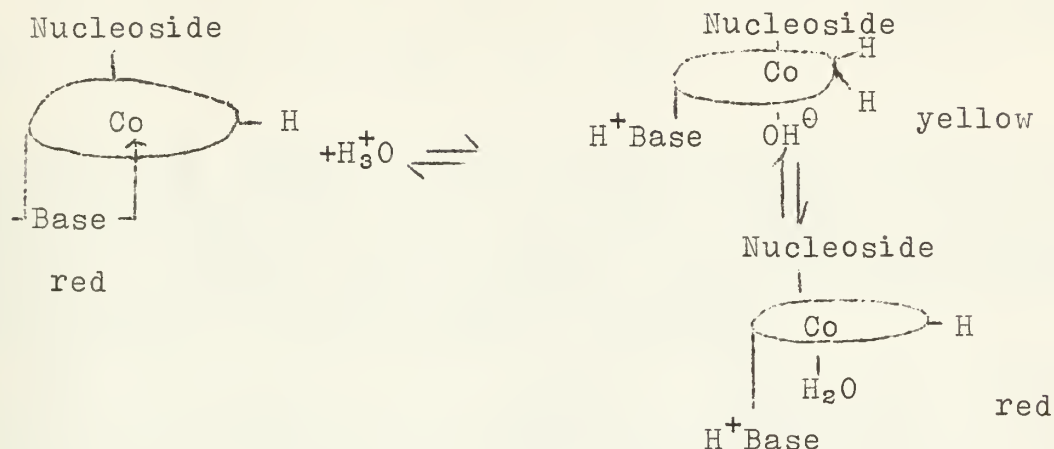
A variety of yellow Corphyrins are known. The yellow Corphyrins show absorption bands in certain definite regions which differ from the red Corphyrins. The following band designation has been proposed; Y_1 (450-500 m μ), Y_2 (400-420 m μ) and Z (300-350 m μ). In general the yellow Corphyrins can be obtained from the red form by acidification; conversely, yellow solutions can be converted to red by raising the pH. The spectral difference between the two forms indicates a fundamental change in the structure of the chromophore, the corrin ring. Therefore the red-yellow shift is attributed to a ring protonation:



Protonation may occur at any of the methene carbon atoms, C_5 , C_{10} or C_{15} , with consequent break in the conjugated system and a shift in the absorption bands to shorter wavelength. The Y_1 band has been correlated with protonation of C_5 and C_{15} and the Y_2 band with protonation of C_{10} . In most cases the nucleotide base is also protonated upon acidification and removed from the coordination sphere.

Coenzyme B_{12} also exists in two forms, red in alkaline and yellow in acid solution. One proton is involved in the change in the chromophore and the yellow solution always shows low intensity bands which may be due to the red species.

Therefore the following equilibrium has been proposed:



The equilibrium between the two protonated forms is independent of pH. The synthetic carbanion-Corphyryns also show similar spectral properties (10).

Optical rotatory dispersion (13) (O.R.D) and circular dichroism (14) (C.D.) studies were undertaken in conjunction with spectral studies. Vitamin B₁₂ shows a positive Cotton effect at $\sim 430 \text{ m}\mu$ and a more intense negative Cotton effect at $\sim 520 \text{ m}\mu$. Replacement of the CN^- by a water molecule does not alter the O.R.D. curve. However in strong acid, a more intense negative Cotton effect appears at $\sim 480 \text{ m}\mu$ and a lower intensity positive Cotton effect appears at $\sim 430 \text{ m}\mu$. The C.D. curve of Vitamin B₁₂ shows a strongly negative band at $360 \text{ m}\mu$, which is particularly sensitive to substituents on the cobalt atom, in addition to bands at $430 \text{ m}\mu(+)$ and $500 \text{ m}\mu(-)$. The dicyano derivative, CN^- replacing the nucleotide base, shows additional bands at $310 \text{ m}\mu(-)$ and $400 \text{ m}\mu(+)$. In strongly acid solution B₁₂ has C.D. bands at $360(+)$, $430(+)$ and $480(-)\text{m}\mu$. The band at $360 \text{ m}\mu$ inverts upon protonation of the vitamin, possibly indicating an inversion of the ring conformation. The data from the O.R.D. and C.D. experiments are consistent with the scheme put forth above for the absorption spectra of the Corphyryns.

REACTIONS OF THE CORPHYRINS (11)

The rate of replacement of the CN^- in B₁₂ by other ligands varies widely and in some cases is instantaneous, in marked contrast to the usual diamagnetic cobalt(III) complexes where ligand exchange is relatively slow. Also the nucleotide base may be replaced by strong ligands such as CN^- and by treatment with concentrated acid. Finally, attempted removal of the cobalt

atom from the structure only results in decomposition of the vitamin. The bond distances obtained from the x-ray structure also demonstrate that the cobalt atom forms four strong bonds with the pyrrole nitrogens in the planar corrin ring and two weaker bonds above and below this plane.

Catalytic hydrogenation of Vitamin B_{12} as well as treatment with stannous chloride in acid yields a paramagnetic yellow-brown compound, B_{12R} , (15) while reduction of B_{12} by sodium borohydride in alkaline solutions produces a diamagnetic grey-green compound, B_{12S} . Sulphite also reduces B_{12R} , H_2O replaces CN^- , to give a Sulphito- B_{12R} complex. This behavior may be typical of sulfur ligands in general.

The corrin ring is not completely planar in the Corphyrins; the C_5 , C_6 and N_{21} atoms are pushed out of the plane of the molecule (4) presumably by steric interaction with the nucleotide base. The strain may further be relieved by inclining rings A and B toward C and D at the C_{10} atom. This makes the attainment of a tetrahedral environment for the trigonal C_{10} atom quite easy and creates an incipient carbonium ion or carbanion. Evidence of the enhanced reactivity of the C_{10} position is the fact that protonation, chlorination (16) and methylation occur at this site. Under certain conditions the C_8 position in ring B is also activated, cyclization of the acetamide group (C_7) at C_8 to form lactam and lactone occurs upon alkaline oxidation and upon treatment with chloramine T (16).

Apparently the naturally occurring form of the vitamin is the Coenzyme B_{12} . In the previous isolation of the vitamin the nucleoside was removed and replaced by CN^- , i.e., Coenzyme B_{12} is attacked by CN^- either aerobically or anaerobically to yield the vitamin derivative (20). The corrin ring in the coenzyme reacts differently than in the vitamin, e.g., it fails to undergo lactam and lactone formation under similar conditions to that of the vitamin (17). Also protonation of the methene carbon occurs at a much higher pH than in the vitamin and in some cases is not removed in strongly alkaline solution. The strong field carbanion ligand, due to its labilizing trans effect, causes the nucleotide base to be less tightly bound and it is readily displaced by a reacting species. In addition, models show that one of the pyrrole rings may become approximately perpendicular to the plane of the other three rings. This affords a means of lengthening the cobalt-nitrogen distance to accommodate a transferable group (18). A number of the Corphyrins which have cobalt bound to an atom of low electronegativity are photo sensitive. The Coenzyme B_{12} is stable to oxygen in the dark but is anaerobically photolyzed to B_{12R} (8). The synthetic carbanion Corphyrins are photolyzed in this manner although some of them are markedly less sensitive (10). Vitamin B_{12} is also unstable

in light and readily forms B_{12a}. Lastly the sulphito Corphyrin, or sulfonic acid derivative with a cobalt-sulfur bond, also undergoes photolysis similar to the coenzyme (19), although other reactions are markedly different (21).

CONCLUSION

Since the discovery of the Corphyrins there has been an extensive effort to discover biochemical processes which they mediate. A large number of these have been found and in a few cases mechanisms for the action of the Corphyrins have been suggested. Nevertheless the precise role they play in biochemical reactions is little understood.

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THE CHEMICAL BEHAVIOR OF THE GROUP VIII ELEMENTS

V. Alan Mode

October 15, 1963

INTRODUCTION

The recent synthesis of various rare gas compounds has required a critical examination of many long-standing principles of synthetic and theoretical inorganic chemistry. Within a few months, rare gas chemistry has developed into a major research effort in many laboratories. Some 100 papers have appeared in the literature in this short period.

EARLY EXPERIMENTS

Many compounds that incorporate one or more atoms of a rare gas into their structures are known, but a true chemical bond is not formed. All of the reported species are classed as clathrate, or cage structures (1,2). There are a few reports of failures to synthesize argon and xenon compounds (3,4). The one product previously claimed as a successful synthesis (5) was shown to be a mixture of inorganic compounds (6). In 1933, Pauling predicted the possible existence of three rare gas fluorides (7); one of these, XeF_6 , has been identified.

CURRENT SYNTHETIC WORK

After Bartlett's combination of xenon with PtF_6 (8), a surge of work has produced a number of rare gas compounds. The syntheses of xenon di-, tetra-, and hexafluorides have been accomplished by the direct reaction of the elements (9-17), by electric discharge (18-20), and by photochemical methods (21).

As the usual analysis involves aqueous hydrolysis of the xenon fluorides, various oxy-species have been studied (22-24), with XeO_3 (24,25), XeOF_4 (26), Ba_2XeO_6 and Na_4XeO_6 (27,28) having been isolated as stable solids from solution. One compound involving a group IV element has been tentatively identified as Xe_2SiF_6 (29).

The synthesis of rare gas compounds other than those involving xenon has been much slower, with just two fluorides of krypton, KrF_2 and KrF_4 , positively isolated (30).

STRUCTURAL AND PHYSICAL PROPERTIES

With the synthesis of each rare gas compound, the determination of structure became of prime importance. Due to their analytical use, infrared (9-13,21,25,26,31,32,64) and Raman (13,26,31) studies have been extensive. In the past

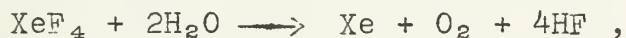
few months, electron and X-ray diffraction (33-37), as well as neutron diffraction (38,39) work has provided a fairly complete picture of two of the xenon compounds. A summary appears below:

	Structure		Xe-X Bond Length (37)	
	<u>molecule</u>	<u>crystal</u>	<u>range</u>	<u>accepted</u>
XeF ₂	linear	body-centered tetragonal	1.7-2.14	2.00
XeF ₄	sq. planar	monoclinic	1.92-1.95	1.95
XeF ₆				1.91
XeO ₃			1.76	

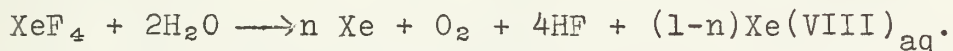
Other physical studies include U-V spectra (40,41), NMR (42,43), ESR (44), conductance (45), magnetic susceptibility studies (16,46,47), and one Mossbauer spectrum (48).

CHEMICAL STUDIES

Other than syntheses, the major chemical interest has been in the aqueous solutions of xenon compounds. The reaction of xenon fluorides in basic solution:



has been of analytic importance (9,24) and the reaction in acidic solution has provided a source of xenon cations (9,10, 24,27,45,49,50):



A number of xenon compounds, such as XeO₃ (22,24,25,35), perxenate salts (7,28,29,50), and oxyfluorides (26,27) have been isolated, although specific chemical reactions have not yet been formulated. Further evidence for a Xe(I) has been reported (29) and a Xe(II) species has been proposed (50) to explain recent experimental observations.

THEORETICAL STUDIES

Naturally the major theoretical interest in the rare gas compounds has been in describing the bonding. This may be divided into three classes: Lewis-electron pair (13,51-54), qualitative quantum mechanical methods (55), and molecular orbital descriptions (40,56-59). Although recent theoretical studies on some isoelectronic polyhalogen anions (60) support the molecular orbital description, no one bonding system has correctly described all of the known rare gas compounds. Attempts have been made at calculating thermodynamic values for the group VIII compounds (61-63), but these are all rather qualitative.

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INFRARED ANALYSIS OF FORMATION CONSTANTS IN AQUEOUS SOLUTION:
APPLICATION OF A NEW METHOD TO NICKEL(II) CYANIDE AND MIXED
CYANIDE-HALIDE SYSTEMS

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October 29, 1963

INTRODUCTION

It is interesting to note that the first known coordination complex prepared was a cyanide complex of iron(II), $K_4[Fe(CN)_6]$, synthesized in 1704 by the German Diesbach (1). Since that time, several transition metal cyanide complexes have been prepared, and discussions of bonding, stereochemistry, and stability have been presented (2)(3).

Cyanide complexes of Ag(I), Au(I), Cu(I), Hg(II), Cd(II), Zn(II), and Ni(II) have recently been observed and characterized by their infrared spectra (4-8). In conjunction with this, a resume by F. H. Khalil should be considered (9).

In general, concentration formation constants of these cyanide complex species have been determined by measurement of an appropriate absorption resulting from an asymmetric cyanide stretching mode in the 2000 - 2200 cm^{-1} region. In the case of Ni(II) cyanide and mixed cyanide-halide complexes, however, a new method has been devised. The resulting formation constant values can be considered accurate to approximately 10%, based on experimental errors and assumptions. The computational scheme described below offers the advantage that it is somewhat more rapid than other methods, as well as the fact that direct proof of complex species formation, i.e. a new absorption band, is used to obtain data.

Some examples of aqueous cyanide complex species investigated by infrared techniques are the following:

$[Ag(CN)_2]^-$, $[Ag(CN)_3]^{2-}$, and $[Ag(CN)_4]^{3-}$ (4):

The successive formation of the tri- and tetra-cyano species is easily seen in the 2050 to 2150 cm^{-1} region of the spectrum. As successive amounts of KCN are added to $KAg(CN)_2$ aqueous solution, there is a steady increase and then diminution of a peak corresponding to the species $[Ag(CN)_3]^{2-}$, and an increase in a peak due to $[Ag(CN)_4]^{3-}$. Table 1 gives the asymmetric cyanide stretching frequencies and extinction coefficients for the appropriate species.

Table 1

Aqueous Species	ν , cm^{-1}	ϵ , $\text{moles}^{-1} \text{ liters cm}^{-1}$
$[\text{Ag}(\text{CN})_2]^-$	2135 ± 1	264 ± 12
$[\text{Ag}(\text{CN})_3]^{2-}$	2105 ± 1	397 ± 23
$[\text{Ag}(\text{CN})_4]^{3-}$	2092 ± 1	556 ± 83
CN^-	2080 ± 1	29 ± 1

Concentrations of the appropriate species were determined from the Bouguer-Beer Law, and dissociation constants for the tri- to di-cyano and tetra- to tri-cyano species were calculated. These values are listed in Table 2.

Table 2

Equilibrium Constants $K_{4,3}$ and $K_{3,2}$ for $\text{Ag(I)}-\text{KCN}-\text{H}_2\text{O}$ System

Equilibrium	Constant
$[\text{Ag}(\text{CN})_3]^{2-} = [\text{Ag}(\text{CN})_2]^- + \text{CN}^-$	0.113
$[\text{Ag}(\text{CN})_4]^{3-} = [\text{Ag}(\text{CN})_3]^{2-} + \text{CN}^-$	3.18

Molar activity coefficients and thermodynamic equilibrium constants were also calculated in this study.

$[\text{Au}(\text{CN})_2]^-$ (4):

Only one cyanide absorption was observed in solutions containing CN/Au ratios of 2 to 10, occurring at $2147 \pm 1 \text{ cm}^{-1}$. The extinction coefficient does not differ in solutions of 0.5 f Au(I) ($\text{CN}/\text{Au} = 2$) and 0.25 f Au(I) ($\text{CN}/\text{Au} = 5$), the value being $477 \pm 25 \text{ mole}^{-1} \text{ liter cm}^{-1}$. The absorption maximum does not shift under these conditions, hence the conclusion was that no other complex cyanide species exist.

$[\text{Cu}(\text{CN})_2]^-$, $[\text{Cu}(\text{CN})_3]^{2-}$, and $[\text{Cu}(\text{CN})_4]^{3-}$ (5):

Copper (I) exhibits a behavior similar to Ag(I) with respect to formation of cyanide complexes. $\text{Cu}(\text{CN})_2^-$, however, has a low extinction coefficient, hence the general trend as in the silver case is not observed. Instead, only the tri- and tetra-cyano species are evident in $\text{KCN}-\text{CuCN}-\text{H}_2\text{O}$ solution spectra. $\text{Cu}(\text{CN})_2^-$ can be observed, however, by addition of HNO_3 to a $\text{NaCN}-\text{CuCN}-\text{H}_2\text{O}$ solution just until precipitation occurs, at which time a weak absorption due to the di-cyano species can be observed. Table 3 indicates the appropriate vibrational frequency and extinction coefficient for each species.

Table 3

Aqueous Species	ν , cm^{-1}	ϵ , $\text{moles}^{-1} \text{ l. cm}^{-1}$
$[\text{Cu}(\text{CN})_2]^-$	2125 ± 3	165 ± 25
$[\text{Cu}(\text{CN})_3]^{2-}$	2094 ± 1	1090 ± 10
$[\text{Cu}(\text{CN})_4]^{3-}$	2076 ± 1	1657 ± 15

The resulting dissociation constants, averaged over approximately fifty determinations each, are listed in Table 4.

Table 4

Equilibrium Constants $K_{4,3}$ and $K_{3,2}$ at 29°C for $\text{Cu(I)}-\text{CN}-\text{H}_2\text{O}$ System

Equilibrium	Constant
$[\text{Cu}(\text{CN})_3]^{2-} = [\text{Cu}(\text{CN})_2]^- + \text{CN}^-$	$(2.44 \pm 0.36) \times 10^{-5}$
$[\text{Cu}(\text{CN})_4]^{3-} = [\text{Cu}(\text{CN})_3]^{2-} + \text{CN}^-$	$(7.6 \pm 0.5) \times 10^{-3}$

$[\text{Hg}(\text{CN})_4]^{2-}$, $[\text{Hg}(\text{CN})_3]^-$, $\text{Hg}(\text{CN})_2$, $[\text{Hg}(\text{CN})_2(\text{OH})]^-$, $[\text{Hg}(\text{CN})_2\text{Cl}]^-$, Hg_2CN , $\text{Hg}_3(\text{CN})_2$, HOHgCN and $[\text{Hg}(\text{CN})_3\text{Cl}]^{2-}$ (6):

An infrared investigation of $\text{Hg(II)}-\text{CN}-\text{H}_2\text{O}$ and $\text{Hg(II)}-\text{CN}-\text{CH}_3\text{OH}$ systems, in addition to solutions also containing halide ions, has revealed several cyanide, cyanide-hydroxide, and cyanide-halide species. Several of these species have also been observed previously by other methods, and formation constants have been calculated for many species. Two points are especially interesting in this series: (a) no infrared absorption for the species HgCN^+ has been observed, (b) an approximation was presented for the calculation of the contribution of one peak to the peak height of an overlapping absorption. This latter point can be considered as a possible extension of the theory developed under the description of the Ni(II) systems. Table 5 lists the absorption maxima of the anionic Hg(II) species observed in this study.

Table 5

Aqueous Species	ν , cm^{-1}
$[\text{Hg}(\text{CN})_4]^{2-}$	2143
$[\text{Hg}(\text{CN})_3]^-$	2161
$[\text{Hg}(\text{CN})_2\text{OH}]^-$	2180
$[\text{Hg}(\text{CN})_2\text{Cl}]^-$	2189
$[\text{Hg}(\text{CN})_3\text{Cl}]^{2-}$	2157 (approx.)

$[\text{Cd}(\text{CN})_3]^-$, $[\text{Cd}(\text{CN})_3\text{Cl}]^{2-}$, and $[\text{Cd}(\text{CN})_2\text{Cl}]^-$ (6):

There has been some conflicting evidence regarding the formation of $\text{Cd}(\text{CN})_6^{4-}$ from $\text{Cd}(\text{CN})_4^{2-}$ in KCN solutions. The infrared absorption of $\text{Cd}(\text{CN})_4^{2-}$ occurs at 2140 cm^{-1} ($\epsilon = 75 \text{ mole}^{-1} \text{ l. cm}^{-1}$) and can be used to detect formation of higher cyano species in solution, assuming appreciable extinction coefficients. Solutions were prepared ranging up to 6M KCN ($\text{K}_2\text{Cd}(\text{CN})_4$ concentration at its maximum) and no shift in peak position or appearance of a new peak was observed.

In the system $\text{Cd}(\text{CN})_2\text{-KCN-H}_2\text{O}$, however, an absorption corresponding to $\text{Cd}(\text{CN})_3^-$ was observed. The mixed ligand complexes $\text{Cd}(\text{CN})_2\text{Cl}^-$ and $\text{Cd}(\text{CN})_3\text{Cl}^{2-}$ were also observed upon the addition of Cl^- . The appropriate absorption bands are indicated in Table 6.

Table 6

Aqueous Species	ν , cm^{-1}
$[\text{Cd}(\text{CN})_4]^{2-}$	2140
$[\text{Cd}(\text{CN})_3]^-$	2148
$[\text{Cd}(\text{CN})_2\text{Cl}]^-$	2147
$[\text{Cd}(\text{CN})_3\text{Cl}]^{2-}$	2145

$[\text{Zn}(\text{CN})_4]^{2-}$ (6):

The 2149 cm^{-1} absorption band ($\epsilon = 113 \text{ mole}^{-1} \text{ l. cm}^{-1}$) of $\text{Zn}(\text{CN})_4^{2-}$ can be used to determine the possibility of $\text{Zn}(\text{CN})_3^-$ formation, by lowering the CN/Zn ratio below 4:1. This results in precipitation of $\text{Zn}(\text{CN})_2$ rather than formation of the tri-cyano species with the reduction of the $\text{Zn}(\text{CN})_4^{2-}$ peak. Hence, infrared techniques can again be used to establish the formation or lack of formation of a particular species.

To this point, the use of infrared spectroscopy has been demonstrated for both the qualitative and quantitative determination of aqueous cyano species of some transition metals.

Ni(II) Systems:

A more specific application of the use of quantitative infrared techniques has been made by Penneman, et al. (7-8).

By use of the method of continuous variations using data taken from the visible region of the spectrum, evidence was found for only one complex of cyanide to Ni(II) ratio greater than four, namely $\text{Ni}(\text{CN})_5^{3-}$. This was confirmed by infrared analysis, where a new peak at $2102 \pm 2 \text{ cm}^{-1}$ was observed. Variation of the peak over a hundredfold range of dilution established the stoichiometry.

Two papers by Blackie and Gold (10,11), however, support the assumption that $\text{Ni}(\text{CN})_4^{2-}$ is quantitatively converted to $\text{Ni}(\text{CN})_6^{4-}$ in solutions containing excess CN^- . This investigation was carried out by proton relaxation techniques, however, and was not found reproducible by Hume (12). Bjerrum also finds evidence (13) for formation of $[\text{Ni}(\text{CN})_5]^{3-}$, $[\text{Ni}(\text{CN})_4(\text{SCN})]^{3-}$, $[\text{Ni}(\text{CN})_4\text{I}]^{3-}$ and $[\text{Ni}(\text{CN})_4\text{Br}]^{3-}$, and indicates a "salt effect" for NO_3^- , Cl^- , and F^- on the $\text{Ni}(\text{CN})_4^{2-}$ species in a spectrophotometric study in the visible region of the spectrum.

The following is a description of a quantitative infrared technique devised by R. A. Penneman which has been applied to this problem (8) and can be applied to other systems possessing the general criteria indicated below:

- 1) An absorption in the infrared spectrum corresponding to one solution species.
- 2) A "window" in the water spectrum to permit use of this absorption.
- 3) An extinction coefficient sufficiently large and a solubility sufficiently great that the peak corresponding to the species is useful.
- 4) Knowledge of the extent of overlap, if any, of the peak.

A further check of the method is available, of course, if the appearance of a new peak concurrent with the diminution of another peak can be also used as an independent means of formation constant calculation.

EXPERIMENTAL

The systems $\text{Ni}(\text{CN})_4^{2-}$ -NaCN- NaClO_4 and $\text{Ni}(\text{CN})_6^{4-}$ -NaCN- NaClO_4 -NaCl were investigated by observation of the cyanide stretching frequencies of the complex species at 2103 and 2124 cm^{-1} using cells prepared from CaF_2 flats with 2-mil Ta spacers. A Perkin-Elmer Model 421 Spectrophotometer was utilized (double beam) to record the spectra. Although spectra were also run in ammoniacal solution, only the aqueous systems and their quantitative relationship to the theory will be discussed here.

RESULTS

The growth of the $\text{Ni}(\text{CN})_6^{4-}$ species peak at 2103 cm^{-1} can be followed by successive addition of NaCN to $\text{Na}_2\text{Ni}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ aqueous solutions. For purposes of calculation, the ionic strength was maintained constant at 4.0 with NaClO_4 substituted for NaCN in varying amounts, and the total Ni(II) concentration was maintained constant at 0.075 M. The optical density of each solution (CN^- concentration ranging from 0 to 3.6M, approx. 20 solutions) was measured at 2103 and 2124 cm^{-1} (the peaks initially thought to correspond to $\text{Ni}(\text{CN})_5^{3-}$ and $\text{Ni}(\text{CN})_4^{2-}$, respectively).

To describe the equilibrium $\text{Ni}(\text{CN})_4^{2-} + \text{CN}^- = \text{Ni}(\text{CN})_5^{3-}$, define the symbols:

(IV)_o = initial concentration of $[\text{Ni}(\text{CN})_4]^{2-}$

(IV) = equilibrium concentration of $[\text{Ni}(\text{CN})_4]^{2-}$

(V) = equilibrium concentration of $[\text{Ni}(\text{CN})_5]^{3-}$

$K_5 = (\text{V})/(\text{IV})(\text{CN}^-)$

Now $(\text{IV})_o = (\text{IV}) + (\text{V})$

from consideration of total Ni(II) in solution. Upon substitution, this yields:

$$(\text{IV})_o = (\text{IV}) + K_5(\text{IV})(\text{CN}^-)$$

and upon rearrangement gives:

$$\frac{1}{(\text{IV})} = \left[\frac{1}{(\text{IV})_o} \right] [1 + K_5(\text{CN}^-)] \quad [1]$$

A plot of Equation [1] shows deviation from linearity at CN^- concentrations above 2.5M, indicating that the residual tetra-cyanide is smaller than predicted by this equation. If one assumes equilibrium between IV, V, and VI (VI defined in a manner analogous to the above species), Equation [2] results from the same reasoning process.

$$\left[\frac{(\text{IV})_o - (\text{IV})}{(\text{IV})} \right] \frac{1}{(\text{CN}^-)} = K_5 + K_5 K_6 (\text{CN}^-) \quad [2]$$

A plot of this equation fits the observed data, giving the values of K_5 and K_6 at $\mu = 4$ found in Table 7. $K_5 \text{Cl}$ is included for later reference.

Table 7
Equilibrium Constants for the Ni(II) System

K_5	0.279 ± 0.008	mole ⁻¹ l.
K_6	0.095 ± 0.013	mole ⁻¹ l.
$K_5 \text{Cl}$	0.22 ± 0.03	mole ⁻¹ l.

It is interesting to note that in this system only two peaks are observed. It can be shown that the $\text{Ni}(\text{CN})_6^{4-}$ species absorbs at approximately 2105 cm⁻¹, hence unresolvable from the $\text{Ni}(\text{CN})_5^{3-}$ species at 2103 cm⁻¹. Therefore, all data must be taken at the 2124 cm⁻¹ peak of $\text{Ni}(\text{CN})_4^{2-}$, relating

its decrease to increased cyanide, penta- and hexa-cyano species concentration as shown above. Hence the method is applicable so long as stoichiometric relationships between species as well as a "useable" peak are available. In this connection, the approximation indicated above under the Hg(II) systems might be used, although unnecessary here.

When NaCl is substituted for NaClO₄ in varying amounts, with the Ni(II) and NaCN concentrations constant at 0.075M and 2.0M, respectively (total $\mu = 4$) a further decrease in the IV peak is observed along with a rise in the V-VI peak. This behavior can be interpreted as a Cl⁻ medium effect of K₅; however in the light of other Cl⁻-CN⁻-metal ion species described above, a 1:1 complex is expected. This complex could be due to [Ni(CN)₄Cl]³⁻ formation, but a separate study of this equilibrium shows that its formation constant is small compared with the magnitude of others. Consequently, a complex of the composition [Ni(CN)₅Cl]⁴⁻ is proposed, and one can write Equation [3] using the above descriptions.

$$(IV)_0 = (IV) + (V) + (VI) + (VCl)$$

and

$$\frac{(IV)_0}{(IV)} = 1 + K_5(CN^-) + K_5K_6(CN^-)^2 + K_5K_5Cl(CN^-)(Cl^-) \quad [3]$$

At constant CN⁻ concentration, the solutions described above fit a plot of the above equation, yielding $K_5Cl = 0.022 \pm 0.03$ mole⁻¹ l. Note that now there are three absorbing species at approximately 2103 cm⁻¹, namely [Ni(CN)₅]³⁻, [Ni(CN)₆]⁴⁻, and [Ni(CN)₅Cl]⁴⁻, the concentrations of each being determinable from quantitative measurements on the [Ni(CN)₄]²⁻ peak alone.

A further application of this method was made at Los Alamos Scientific Laboratory (14). The effect of other halides on the [Ni(CN)₄]²⁻-CN⁻ equilibria was studied in essentially the same manner as described above for the Cl⁻ work. Although the data analysis is not complete at this time, it can qualitatively be said that F⁻ exhibits a more pronounced effect on the above equilibria than does Cl⁻, yielding a formation constant for [Ni(CN)₅F]⁴⁻ significantly higher than that involving Cl⁻. Again, a negligible effect on the Ni(CN)₄²⁻ species was observed. Preliminary work with Br⁻ and I⁻ shows progressively weaker interactions with the Ni(CN)₅³⁻ species. This correlates well with Bjerrum's work (11), however his implied definition of the limit of a "salt effect" seems rather arbitrary. Two difficulties are initially apparent in the F⁻ work, however. Due to the low solubility of NaF in H₂O, KF was chosen for use. However, due to the low solubility of KClO₄, another non-complexing medium was needed to maintain constant ionic strength. NaNO₃ was found not to cause an appreciable change in solution characteristics when compared to NaClO₄, hence KNO₃ was chosen. A second

difficulty was encountered in this substitution, however, as it was noticed that significantly different solution characteristics were observed when K^+ was substituted for Na^+ . Hence, for strict comparison with the Cl^- data, these differences must be resolved. This work is proceeding at the present time.

CONCLUSION

Some of the quantitative and qualitative uses of infrared spectroscopy of aqueous solutions has been described. The theory which has been developed for the treatment of absorption data can be utilized in systems displaying the general characteristics described above. The system need not include cyanide species, of course, so long as an appropriate window is available in the H_2O spectrum within which one can observe spectra corresponding to the species in solution. In this connection, a summary by R. H. Carlson (15) is applicable. The approximation indicated under $Hg(II)$ and $Ni(II)$ species above for overlapping peak contributions can be used in conjunction with the described theory. Equations [1-3] are sufficiently general to indicate the appropriate steps required for the derivation of equations involving other species, for example the hypothetical ion $[Ni(CN)_4Cl_2]^{4-}$. The method is general, and accurate to approximately 10%, indicating its usefulness as a rapid indication technique for formation constant determinations.

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STEREOCHEMISTRY OF LANTHANON IONS
IN CRYSTALS

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November 19, 1963

I. INTRODUCTION

Crystal structures are known for numerous lanthanon compounds. These ions are interesting on account of their high coordination numbers. Here we will survey the data for compounds of known structure (excluding compounds of metallic nature), and consider the effect of relative ion sizes in determining the coordination of the metal ion.

II. THEORY

One can calculate limiting radius ratios for given coordination number (C.N.) and geometry. These ratios set a minimum on the size of any metal ion in a given coordination polyhedron involving ligands of a given size. Below is a table giving results of such calculations.

TABLE 1^a

C.N.	Geometry	Limiting Radius Ratio	Min. Cation Radius for Given Anion (Å)				
			O (1.35A)	F (1.33A)	Cl (1.80A)	Br (1.96A)	I (2.20A)
4	Tetrahedron	0.225	0.30	0.30	0.41	0.44	0.50
6	Octahedron	0.414	0.56	0.55	0.75	0.81	0.91
6	Trigonal Prism	0.528	0.71	0.70	0.95	1.03	1.16
8	Square Antiprism	0.645	0.87	0.86	1.16	1.26	1.42
7	Pentagonal Bipyramid	0.701	0.95	0.93	1.26	1.37	1.54
8	Cube	0.732	0.99	0.97	1.32	1.43	1.61
9	Trigonal Prism Plus 3 Additional Ligands Centered on Prism Faces	0.732	0.99	0.97	1.32	1.43	1.61
12	Icosahedron	0.902	1.22	1.20	1.62	1.77	1.98

^aThe anion radii are taken from Ref. 2, Table III-3 (observed values).

Tabulated below are radii of several cations.

TABLE 2^a (Values in Å)

Mg	0.75	Sc	0.83	Si	0.40
Zn	0.83	Ti	0.70	Ge	0.55
Mn	0.83	Cr	0.70	Sn	0.65
Fe	0.80	Fe	0.67	Pb	0.70
Co	0.78	Al	0.55	Ti	0.60
Ni	0.74	Ga	0.65	Mn	0.52

Ca	1.05	In	0.95	Zr	0.80
Sr	1.18	Bi	1.20	Ce	1.01
Ba	1.38	Y	0.95	Th	1.10
Cd	0.99	La	1.15	U	1.05
Pb	1.18	Ce	1.11		
Eu	1.2 ^c	Pr	1.09		
Yb	1.0 ^c	Nd	1.07 ^b		
Tm	1.0 ^d	Sm	1.03 ^b		
Sm	1.2 ^d	Gd	1.01		
Nd	1.3 ^d	Dy	0.97		
		Er	0.94		
		Yb	0.89		
		Lu	0.88		

^aValues are taken mostly from Ref. 2, Table III-3 (observed values)

^bValues for Sm-Lu are taken from Ref. 1, p. 70 (adjusted for consistency)

^cThese ions appear to be about the same size as Sr⁺² and Ca⁺², resp.

^dExtrapolated or interpolated, assuming differences are the same as for corresponding M⁺³ ions.

On inspection of Tables 1 and 2, one can expect Ln^{+3} ions to show a C.N. of 7, 8 or 9 towards O^{2-} or F^- ; and 6 towards Cl^- , Br^- , or I^- .

III. SURVEY OF COMPOUNDS OF KNOWN STRUCTURE

Following are tables of the crystal structures of known lanthanon compounds. The +3, +2, and +4 oxidation states are dealt with in turn.

A. The +3 State

Compound (General Formula)	Structure (Space Group (Type))	Ln Ions	C.N.	Site Sym.	Geometry	Refs.
LnF_3	$\text{P6}_3/\text{mmc}, 2$	La-Eu, Ho, Tm	11	D_{3h}	Fig.1	2,57
LnF_3	$\text{Pnma}, 4$	Sm-Lu, Y	8	C_s	Fig.2	2,57
LnCl_3	$\text{P6}_3/\text{m}, 2$ (UCl_3 type)	La-Gd	9	C_{3h}	Fig.3	2,55,62
LnCl_3	$\text{C2}/\text{m}, 4$	Dy-Lu, Y	6	C_2	Octahedron	2,53
LnBr_3	$\text{P6}_3/\text{m}, 2$ (UCl_3 type)	La-Pr	9	C_{3h}	Fig.3	2,62
LnBr_3	$\text{Cmcm}, 4$ (PuBr_3 type)	Nd, Sm	8	C_{2v}	Fig.2	2
LnI_3	$\text{Cmcm}, 4$ (PuBr_3 type)	La	8	C_{2v}	Fig.2	2
LnI_3	$\text{P3}, 2$ (BiI_3 type)	Y	6	C_3	Octahedron	39
LnOF	$\text{P4}/\text{nnm}, 2$	La, Y	8		Distn. of CaF_2 Structure	2,55,64
LnOF	$\text{R}\bar{3}\text{m}, 2$	La, Pr, Nd, Sm-Tb, Y	8		Distn. of CaF_2 Structure	2,55,64
LnOCl	$\text{P4}/\text{nnm}, 2$ (PbFCl type)	La-Er, Y	9	C_{4v}	Fig.4	54,65
LnOBr	$\text{P4}/\text{nnm}, 2$ (PbFCl type)	Nd	9	C_{4v}	Fig.4	65
LnOI	$\text{P4}/\text{nnm}, 2$	La, Sm, Eu, Tm, Yb	9	C_{4v}	Fig.4	6,7
Ln_2O_3	$\text{P}\bar{3}\text{m}1, 1$	La-Nd	7	D_{3d}	Fig.5	2,59
Ln_2O_3	Mon., 6	Sm-Dy	?			30,60
Ln_2O_3	$\text{Ia}\bar{3}, 16$	Nd-Lu, Y	6 6	C_{3N} C_2	Octahedron Octahedron	2,55,59
KLnF_4	$\text{Fm}\bar{3}\text{m}, 2$	La, Ce	8		CaF_2 Structure	61,65
K_3LnF_6	$\text{I4}/\text{mmm}, 2$	Y	6	D_{4h}	Octahedron	13
Ln_2NiO_4	$\text{I4}/\text{mmm}, 2$	La	9	C_{4v}	Fig.4	17,28,47
LnMO_3	(Perovskite type)	La-Er, Y	12			(f)
$\text{Ln}_3\text{M}_2\text{O}_{12}$	$\text{Fd}\bar{3}\text{c}, 8$ (Garnet type)	La, Gd, Y	8	S_4	Dodecahedron	(1)
$\text{Ln}_2\text{M}_2\text{O}_7$	$\text{Fd}\bar{3}\text{m}, 8$ (Pyrochlore type)	La-Lu, Y	8	D_{3d}		10,11, 15,60

(Continued)

Compound (General Formula)	Structure (Space Group (Type))	Ln Ions	C.N.	Site Sym.	Geometry	Refs.
LnMO_4	$\text{PZ}_1/\text{n}, 4$ (Monazite type)	a, c		C_1		20, 30, 44, 45, 49, 67, 68, 69
LnM_2	$\text{P3}_2, 21-\text{P3}_2, 21, 3$	a, c	8	C_2		
LnMO_4	$\text{I4}_1/\text{amd}, 4$ (Zircon type)	a, d	8	D_{2d}		
LnMO_4	Mon., 4 (Fergusonite type)	b, e	?			
$\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{PZ}_1/\text{n}, 2$	Nd, Sm, Gd, Er	8	C_2	Fig. 6	63
$\text{Ln}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	$\text{P6}_3/\text{c}, 2$	La, Pr-Dy, Er	9	D_{3h}	Fig. 3	31, 48, 51
$\text{Ln}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	$\text{P6}_3/\text{m}, 2$	La	9	C_{3h}	Fig. 3	35
$\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	Mon., 4	Ce-Tm	9?	C_{3i}	Fig. 7	26, 29, 51
$\text{Ln}(\text{EtOSO}_3)_3 \cdot 9\text{H}_2\text{O}$	$\text{P6}_3/\text{m}, 2$	La-Tm, Y	9	D_{3h}	Fig. 3	25, 37, 51
$\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	Tricl., 2	(La, Ce, Pr)	10	$\text{C}_1?$		52, 58
$\text{Ln}(\text{HCO}_2)_3$	$\text{R}\bar{3}\text{m}, 1$	Gd	9		Fig. 3	46
LnBO_3	$\text{Pbnm}, 4$ (Aragonite type)	La, Nd	9	C_s		24, 40, 70
LnBO_3	$\text{Pbnm}, 4$ (Vaterite type)	Sm-Yb, Y	?			
LnBO_3	$\text{R}\bar{3}\text{c}, 2$ (Calcite type)	Lu	6	C_{3i}		
$\text{Ln}_2(\text{WO}_4)_3$	$\text{C2}/\text{c}, 4$	Eu			Deformed CaWO_4 Structure with Vacancies	56
$\text{ULn}_6\text{O}_{12}$	Rhb., 1	Y	(8)		Probably like Tb_7O_{12}	14

^aN = P, As, V, Cr

^bM = Nb, Ta

^cFormed by larger Ln^{+3} ions

^dFormed by smaller Ln^{+3} ions

^eFormed by all Ln^{+3} ions

^fS. Geller and others have published numerous papers on these compounds

B. The +2 State

Compound (General Formula)	Structure (Space Group (Type))	Ln Ions	C.N.	Site Sym.	Geometry	Refs.
LnF_2	$\text{Fm}\bar{3}\text{m}, 4$ (CaF_2 type)	Eu	8	O_h	Cube	3
LnCl_2	$\text{Pnma}, 4$ (PbCl_2 type)	Nd, Sm, Eu	9	C_s	Fig. 3	2, 3, 18
LnBr_2	$\text{Pnma}, 4$ (SrBr_2 type)	Sm, Eu	7	C_s	Fig. 8	3
LnI_2	$\text{Pnma}, 4$ (SrBr_2 type)	Nd	7	C_s	Fig. 8	18
LnI_2	$\text{P}\bar{3}\text{m}1, 1$ (CdI_2 type)	Tm, Yb	6	D_{3d}	Octahedron	3, 5
LnO	$\text{Fm}\bar{3}\text{m}, 4$ (NaCl type)	Sm, Eu, Yb	6	O_h	Octahedron	3
LnSO_4	$\text{Pnma}, 4$ (BaSO_4 type)	Sm, Eu	12	C_s		3
LnSO_4	$\text{P}3_121\text{-P}3_221, 3$ (CePO_4 type)	Yb	8	C_2		3
LnCO_3	$\text{Pbnm}, 4$ (Aragonite type)	Sm, Eu, Yb	9	C_s		3
Ln_3O_4	$\text{Pnam}, 4$ (CaFe_2O_4 type)	Eu	8(Eu^{II}) 6(Eu^{III})		Fig. 2 Distorted Octahedron	8

The compounds SmI_2 , EuI_2 , YbCl_2 , and YbBr_2 are said not to be isomorphous with any of the LnX_2 listed in the table (3). EuI_2 is monoclinic ($\text{P}2_1/\text{c}$), $Z=4$ (ref. 7). YbCl_2 is orthorhombic, supposedly a distorted CaF_2 structure (C.N. = 8) (Ref. 3).

Remy (66) lists a compound $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$. It may be isomorphous with $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$.

The $\text{Eu}(\text{II})$ in Eu_3O_4 is isomorphously replaceable by Sr to give SrEu_2O_4 (8).

C. The +4 State

Ce and Tb form tetrafluorides isomorphous with those of Zr, Th, etc. The crystals are monoclinic ($\text{C}2/\text{c}$, $Z=12$). Since F positions are not available, the coordination is not known, but is probably 7, 8, or 9. (Refs. 2, 17, 55).

Compounds of the type M_2LnF_6 and M_3LnF_7 ($\text{M} = \text{Na}$, K , Rb , or Cs) are known for Ce, Pr and Tb. Many of them seem to be isomorphous with corresponding Th, U, or Zr compounds (coordination numbers 7, 8, or 9) (Refs. 4, 32, 33, 34).

CeO_2 has the CaF_2 structure (CeO_8 cubic coordination) (Ref. 2).

The nonstoichiometric oxides of Ce, Pr and Tb approach the CaF_2 structure in the limit LnO_2 (refs. 12,21, 22,23).

Structures are known for a number of Ce(IV) oxysalts and complexes: $\text{Ce}(\text{IO}_3)_4$ (16); $\text{Ce}(\text{IO}_3)_4 \cdot \text{H}_2\text{O}$ (36); $\text{CeOSO}_4 \cdot \text{H}_2\text{O}$ (41); $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ (42); $\text{Ce}(\text{acac})_4$ and $\text{Ce}(\text{dibenzoylmethane})_4$ (9.43, 50). In all of these compounds, Ce(IV) has C.N. = 8 (distorted archimedean anti-prism).

CeGeO_4 has the CaWO_4 ($\text{I}4_1/\text{a}$, $Z = 4$) structure (19). Ce(IV) has C.N. = 8, site symmetry S_4 .

IV. DISCUSSION OF THE DATA

We tabulate below the coordination number of Ln^{+3} for several compounds.

TABLE 3

The heavy vertical bars indicate where a change in coordination number is expected

Ion (+3)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb	Lu
Radius (Å)	1.15	1.11	1.09	1.07	1.03	1.02	1.01	0.99	0.97	0.96	0.95	0.94	0.92	0.89	0.88
C.N. For:															
LnF ₃	11	11	11	11	11,8	11,8	8	8	8	11,8	8	8	11,8	8	8
LnCl ₃	9	9	9	9	9	9	9	6	6	6	6	6	6	6	6
LnBr ₃	9	9	9	8	8	8	-	-	-	-	-	-	-	-	-
LnI ₃	8	-	-	-	-	-	-	-	-	-	6	-	-	-	-
Ln ₂ O ₃	7	7	7	7,6	6	6	6	6	6	6	6	6	6	6	6
LnBO ₃	9			9											6

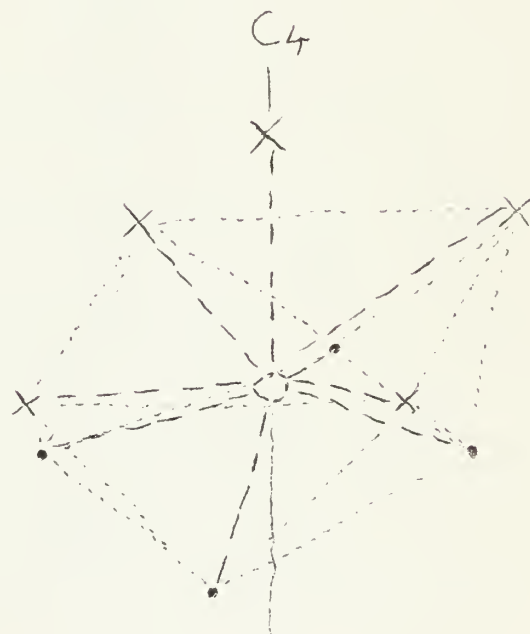
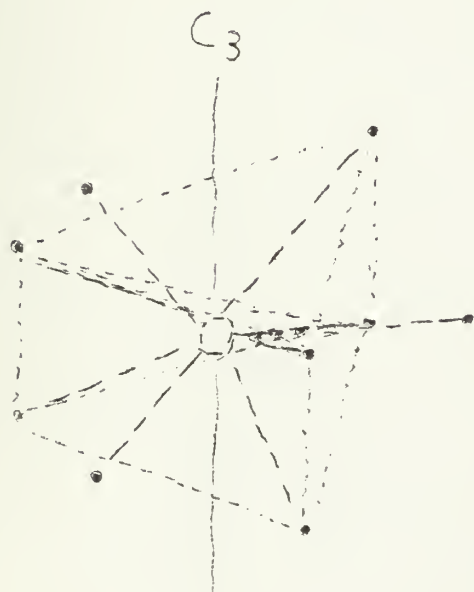
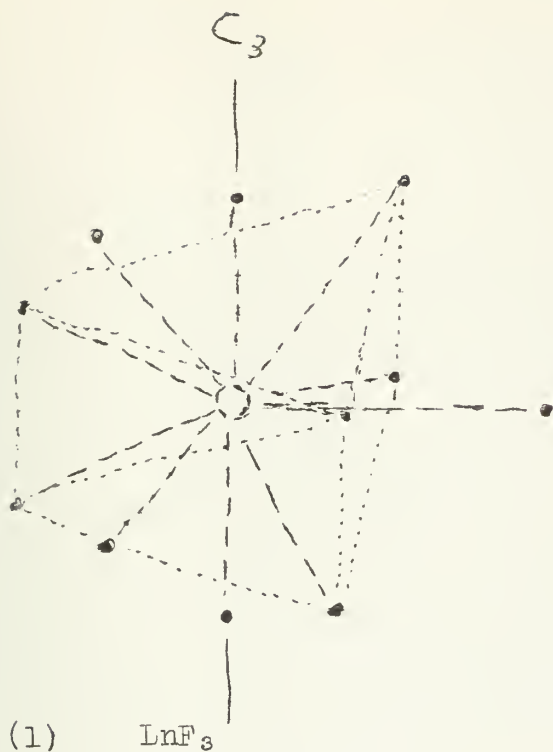
One sees that the theoretically predicted C.N. does not agree well with that observed. However the radius-ratio rule is obeyed qualitatively. The following reasons for the poor quantitative agreement are suggested: (1) The theoretical values are based on the assumption that all the ligands are equidistant from the metal ion. This condition is not fulfilled for the high coordination numbers. (2) The theoretical values are also based on assumption that the structure is built up of ions. If covalency is significant, the effective radii of anion and cation will be smaller and larger, respectively, leading to a tendency toward a higher coordination number.

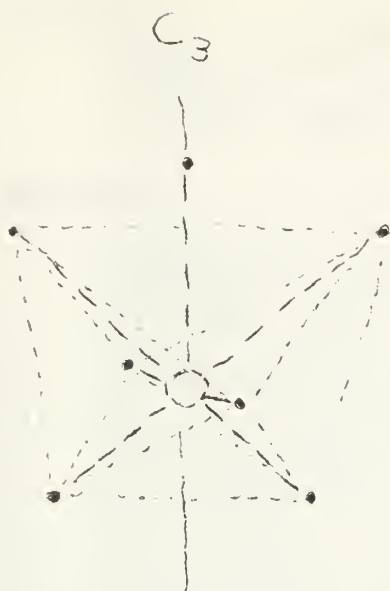
V. CONCLUSION

We have surveyed data on stereochemistry of lanthanon ions in crystals, and have noted that the radius-ratio rule for coordination is obeyed qualitatively.

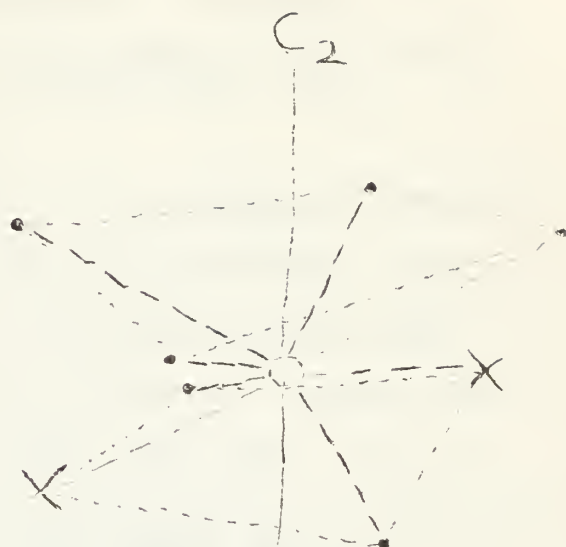
It would be interesting to learn the structures of other lanthanon compounds, e.g. $\text{Ln}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$, $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Ln}(\text{acac})_3 \cdot n\text{H}_2\text{O}$, $\text{Ln}(\text{C}_5\text{H}_5)_3$, and Ln-EDTA complexes.

FIGURES

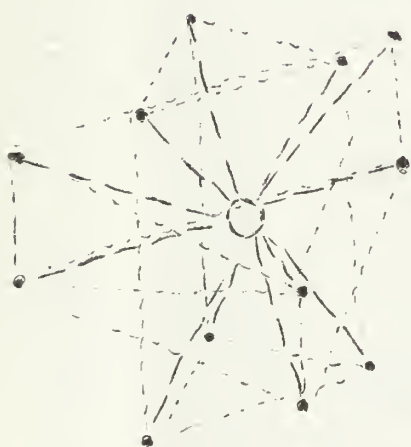




(5) Ln_2O_3



(6) $\text{LnCl}_3 \cdot 6\text{H}_2\text{O} ([\text{Ln}(\text{H}_2\text{O})_6\text{Cl}_2]^{+})$



(7) $\text{Ln}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
 $([\text{Ln}(\text{OH}_2)_6\text{O}_6])$



(8) $\text{LnBr}_2, \text{LnI}_2$

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SOME ASPECTS OF THE MOLECULAR ORBITAL THEORY
OF TRANSITION METAL COMPLEXES

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December 3, 1963

Resumé:

The method of applying the LCAO-MO approximation to transition metal complexes will be examined in detail. Semi-empirical techniques for estimation of various integrals involved, will be compared with available "ab initio" calculations for transition metal complexes. The physical picture which MO theory presents of the nature of the interaction between ligands and central atom, with respect to the magnitude of various energy terms in the molecular Hamiltonian, will be contrasted with a pure crystalline field approach. Finally, the application of the less questionable and most readily accessible aspects of the theory--those deriving from symmetry considerations alone--to the description of electronic absorption spectra will follow.

I. INTRODUCTION

It is not intended that evidence for covalent bonding in transition metal complexes shall be reexamined in this seminar. Suffice it to say that, certain magnetic resonance experiments (ESR, NMR) and absorption band intensities of transition metal complexes are not amenable to interpretation by a model acknowledging the ligands as only producing a point charge or point dipole field causing splitting and mixing of certain degenerate sets of orbitals containing the valence electrons of the central atom. Presumably interpretation of such experiments demands the use of a model which gives a more realistic picture of bonding.

The proposed model is that first introduced by Van Vleck (1). It is a molecular orbital model in that each electron (or more commonly each valence electron) is assigned a one-electron wave function which in general extends over the whole complex. It receives the name LCAO-MO model since the MO's are considered to be made up of some linear combination of atomic orbitals (LCAO) on different centers. Whereas, Crystal Field Theory is a perturbational approach to getting a better wave function for the electrons of interest, the LCAO-MO model uses a variational approach. That is to say, the best LCAO wave function is found by varying the coefficients of the AO's until the energy is minimized. The minimization procedure results in a set of n (the no. of AO's) simultaneous linear equations, whose non-trivial solutions is given by the secular determinant:

$$\text{Det}(H_{ij} - ES_{ij}) = 0$$

II. STEPS IN THE CALCULATION OF THE ENERGY OF THE ONE-ELECTRON MO'S OF THE COMPLEX

A. Construction of the Symmetry Orbitals (2)

This step factors the secular determinant. The symmetry orbitals are constructed in the standard manner. Once sigma and pi type ligand AO's are distinguished, the representation for each type is decomposed under the point group of the molecule. For example, for O_h symmetry:

$$X_{\sigma}, \text{ reducible} = a_{1g} + e_g + t_{1u}$$

$$X_{\pi}, \text{ reducible} = t_{1g} + t_{2g} + t_{1u} + t_{2u}.$$

linear combinations of ligand orbitals must then be formed, which transform according to the above irreducible representations of O_h . The results of such an analysis can be found in Table 1 below. The transformation properties of the metal orbitals are then examined (see Table 1). Finally MO's are formed by combining ligand sets and metal orbitals of the same symmetry, noting that for degenerate representations only like components of the given symmetry species will combine.

Table 1

Symmetry	Central Atom	Ligand σ Orbitals	Ligand π Orbitals
a_{1g}	s	$(1/6)^{1/2}(z_1+z_2+z_3+z_4+z_5+z_6)$	
e_g	$d_{x^2-y^2}$ d_{z^2}	$1/2(z_1-z_2+z_4-z_5)$ $(1/12)^{1/2}(2z_3+2z_6-z_1-z_2-z_4-z_5)$	
t_{1u}	p_x p_y p_z	$(1/2)^{1/2}(z_1-z_4)$ " (z_2-z_5) " (z_3-z_6)	$1/2(x_3+y_2-x_5-y_6)$ " $(x_1+y_3-x_6-y_4)$ " $(x_2+y_1-x_4-y_5)$
t_{2g}	d_{xz} d_{yz} d_{xy}		$1/2(x_3+y_1+x_4+y_6)$ " $(x_2+y_3+x_5+y_4)$ " $(x_1+y_2+x_6+y_5)$

B. Solution of the Secular Determinant

$$\text{Det}(H_{ij} - E G_{ij}) = 0$$

There will be one of these for each irreducible representation present. Solution of these will give the one-electron energy of the MO of the given symmetry, and putting the roots back into the secular equations allow the coefficients of the metal and ligand part of the MO to be determined. Note well that we must solve quadratics for the a_{1g} , e_g and t_{2g} symmetries but a cubic for the t_{1u} species. The latter being due to the fact that two ligand sets occur with t_{1u} symmetry. Thus the t_{1u} type MO will have both σ and π character though in general the π contribution will be much smaller. If the symmetry of the complex is less than O_h the order of the secular equations which must be solved are in general higher.

Let us consider the case of the e_g MO and examine each element in the secular determinant. The e_g MO is in general form:

$$\psi_{eg} = N(\psi_1 + \lambda \psi_2) \quad (\text{for the anti-bonding orbital})$$

$$\text{where } \psi_1 = d_{x^2-y^2}$$

$$\psi_2 = 1/2(z_1 - z_2 + z_4 - z_5) \quad (\text{and } z_i \text{ is a ligand } \sigma \text{ orbital on the } i\text{th ligand and may be a hybrid eg. } z_i = \sin\theta \sin\phi + \cos\theta \cos\phi)$$

The various elements of the secular determinant would then be as follows:

$$(1) \quad H_{ii} = (\psi_i | H | \psi_i)$$

These integrals are strictly not interpretable until we state what the Hamiltonian is. However in a semi-empirical calculation one would like to think of these integrals as resembling free atom or ion orbital energies (for example E_{3d} for $i = 1$ and E_{nsp} for $i = 2$) modified by molecular potential terms due to the presence of the ligands for $i = 1$ and metal ion for $i = 2$. The latter effects might be estimated by techniques such as used by Wolfsberg and Helmholtz, (3) the authors of the first calculations of this nature, or by the use of valence state ionization potentials (VSIP) utilized in more recent calculations (4,5).

The concept of Valence State, and VSIP, was introduced by Van Vleck and Mulliken (6). Its introduction was a result of an attempt to describe the condition of atoms in molecules. In general VSIP are larger than

ground state ionization potential (reflecting the lower potential energy state of a given electron in a molecule compared to its state in the atom). Moffitt (7) using a different but near equivalent approach to that of Mulliken has published formulas for calculating $VSIP$. Jaffe (8) using Mulliken's formulation gives tabulated values for many atoms in various valence states, including hybridized ones. Yet a glance at the papers using this semi-empirical MO approach will show that the guiding principle in the initial estimates is that of the electroneutrality principle, and that ground state IP would probably do nearly as well with adjustment for the charge distribution.

(2) H_{ij}

These off diagonal resonance type integrals are approximated in the semi empirical method according to a suggestion of Mulliken and modified by later workers:

$$H_{ij} = -k(H_{ii}H_{jj})^{1/2} S_{ij}$$

The constant k has been taken as 2 in most recent work. The use of the same k and $VSIP$ for both σ and π interaction usually results in an underestimate of π mixing relative to σ in the wave functions, since differences will then only depend on overlap differences (5).

(3) G_{ij} (or S_{ij})

These are group overlap integrals and the only integrals which can be evaluated directly without recourse to an empirical estimate. For the e_g orbital it takes the form

$$(3d_{x^2-y^2} | 1/2(z_1-z_2+z_4-z_5)).$$

By expanding this can be written in terms of two center overlap integrals for which there are extensive tabulations for Slater type radial functions. Some of interest are presented in Table 2, along with, for comparison, the same integrals calculated using supposedly "better" radial parts for the wave functions, i.e. Hartree-Fock type.

Table 2

Overlap	Hartree-Fock	Slater
$(d_{\sigma} S)$.047	.190
$(d_{\sigma} p_{\sigma})$.064	.165
$(d_{\pi} p_{\pi})$.039	.084
$(\phi_e X_s)$.081	.328
$(\phi_e X_p)$.111	.296
$(\phi_t X_t)$.076	.168

Group and two center overlap integrals for $KNiF_3$, where X_i refers to the ligand set.

Thus using the above semi-empirical estimates, determined for a given starting charge distribution, the individual one-electron MO energies are calculated and the mixing coefficients determined. The new charge distribution is then determined, for example, for the metal atom:

$$q_{\text{new}} = q_{\text{orig.}} - \sum_{i(\text{mo's})} \left[\frac{1 + \lambda_i S_i}{1 + 2\lambda_i S_i + \lambda_i^2} \right] n_i$$

The USTF's are then adjusted for the new charge distribution, e.g. if the metal atom becomes less positive its coulomb integral becomes less negative. This cyclic process is continued until a self consistent result is reached.

III. COMPARISONS

Recently Shulman and Sugano (10) have treated the octahedral complex $(\text{NiF}_6)^{4-}$ occurring in the perovskite, KNiF_3 , by this same molecular orbital method. However they have calculated all integrals involved, using the best atomic wave functions available for the atoms and using no empirical estimates (ab initio). Their results should provide some good tests for our thinking on the empirical estimates used in the above approximate treatment. The results of comparisons between calculated and estimated quantities will be given in the seminar.

The validity of their approach to the calculation is attested to by the good agreement between their calculated values for Dq , the mixing coefficients, the Slater-Condon parameters and the spin-orbit coupling parameter and the experimental values for these quantities. Thus it seems worth noting some of their findings on the nature of the metal-ligand interaction by an MO scheme:

- 1) The covalency admixture of the 2s ligand orbitals as given by the mixing coefficient γ_s , is only about 1/3 as large as the 2S overlap (consult Tables 2 and 4). This can be shown to be a result of the large negative value of the 2S orbital energy $(X_i | H | X_i)$ (see Table 3), since for the bonding orbital^s the mixing coefficient is given by

$$\gamma_i = (-(\phi_i | H | X_i) + S_i (X_i | H | X_i)) / ((\phi_i | H | \phi_i) - (X_i | H | X_i)).$$

- 2) In contrast the $2p\sigma$ and $2p\pi$ covalencies are more than twice the overlap. Yet in the fluorides intuitively expecting σ to be much larger than π one finds their ratio is 1.6 respectively. The origin of this relatively large π covalency is due partly to the lowering of the $2p\sigma$ orbital energy relative to the $2p\pi$ energy in the complex by the attractive potential of the central metal ion.

- 3) Finally it can be shown that π bonding should be important whenever the wave functions themselves are important, i.e., in hyperfine interactions, in optical intensities and in magnetic exchange interaction, but it is not as important as the σ bonding when the bond energy is involved, i.e., in bond distances, bond energy etc.

With the aid of Figure 1, the relative contributions to $10 Dq$ according to this MO approach shall be discussed.

Table 3

Numerical Values of Necessary Integrals in Atomic Units(27.2ev) ⁽¹⁰⁾

Orbital	$(\phi H \phi)$	$(\phi H X)$	$(X H X)$
e_g S	.1202	- .127 { - .116 - .097	- .239 { - .996 - .163
σ			
t_{2g} π	.1365	-.044	-.084

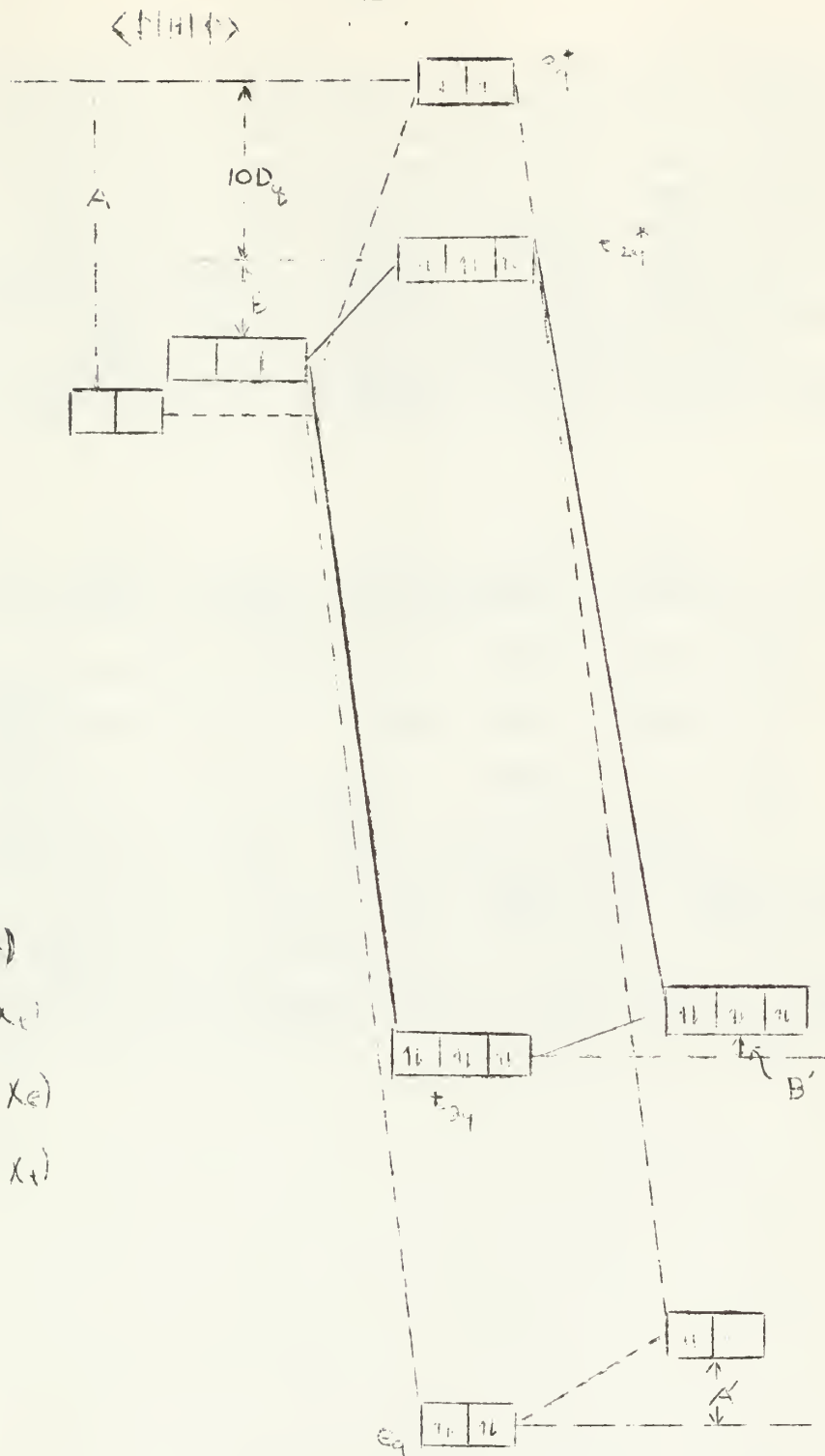
Table 4

Values of the Mixing Coefficient for $(NiF_6)^{4-}$

	γ (bonding)	λ (antibonding)
e_g S	.113 { .031 .285	.412 { .113 .396
σ		
t_{2g} π	.173	.249

IV. APPLICATIONS

The exact relation between the ab initio calculations discussed herein and the results of the semi-empirical treatment of the same complex can not be clearly delineated without more thought on the matter and use of computer facilities to use the cyclic procedure in the latter method to full advantage. Thus only the symmetry analysis aspect of MO theory will be used in what follows.



$$A = \lambda_e(\phi_e | h | \chi_e)$$

$$B = \lambda_e(\phi_e | h | \chi_e)$$

$$A' = \lambda_e(\phi_e | h | \chi_e)$$

$$B' = \lambda_e(\phi_e | h | \chi_e)$$

$$\lambda = \gamma + S$$

Figure: Energy-level diagram for molecular electronic states formed between $1g$ and $2g$ and $1u$ and $2u$ depends

The isoelectronic hexacyanides and hexacarbonyls have been treated recently by the LCAO -MO method (11). They present an interesting area of investigation as for their electronic absorption spectra since they have large values for $10Dq$ and this causes their primarily d-d transitions to occur in the region of their charge transfer transitions. Moreover with these types of ligands (having available low energy antibonding acceptor orbitals) a good possibility of seeing the two major types of charge transfer transitions is present. In addition from our understanding gained from the MO results on the fluorides, we might be able to rationalize some trends in Dq and the charge transfer spectra.

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INORGANIC LINKAGE ISOMERISM OF THE THIOCYANATE ION⁽¹⁾

John L. Burmeister

I. INTRODUCTION

This study was concerned with what is, perhaps, the least familiar of the types of isomerism⁽²⁾ found in inorganic coordination chemistry, namely, linkage isomerism. Linkage isomerism occurs whenever a given ligand can attach itself to the same central metal atom by bonding through either one of two different atoms within the ligand. For true linkage isomerism, all other factors, such as the geometrical configuration and percentage composition of the resulting complexes, must remain the same.

Prior to this work, the only ligand known to exhibit this type of isomerism was the nitrite ion, NO_2^- . The first example was reported in 1893 by Jørgensen⁽³⁾, who isolated the nitro (Co-NO_2) and nitrito (Co-ONO) pentammines of cobalt(III). More recently, Basolo and Hammaker^(4,5) succeeded in extending nitro-nitrito linkage isomerism to include the pentammines of rhodium(III) iridium(III) and platinum(IV).

The thiocyanate ion, $:\text{N}\equiv\text{C}-\ddot{\text{S}}:^-$, presents itself as the most logical candidate for a second example of linkage isomerism. It is known to form both thiocyanato (M-SCN) and isothiocyanato (M-NCS) complexes, depending on the central metal atom employed⁽⁶⁾, as well as bridged (M-SCN-M) species⁽⁷⁾. Several workers^(8,9) have pointed out that the change from M-NCS to M-SCN bonding coincides approximately in the periodic table with the change in the relative bonding strengths of the halide ions from $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ to $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$. The first order is followed by halogeno complexes of metals of the first transition series, the second order by halogeno complexes of metals to the right of Group VII in the second and third transition series, the class (a) and class (b) acceptors, respectively, proposed by Ahrlund, Chatt and Davies⁽¹⁰⁾ for the coordination of metal ions with an extensive series of ligands. Several explanations have been proposed for this change^(10,11,12). The generalization of thiocyanate bonding given above applies only to complexes wherein thiocyanate is the sole ligand.

II. DETERMINATION OF THE MODE OF THIOCYANATE BONDING

To differentiate among the three types of thiocyanate bonding, three tools may be employed: X-ray crystallography, visible spectra, and infrared spectra. X-ray crystallography, although offering the most definitive answer, is the least convenient, in that it is quite time consuming, and requires

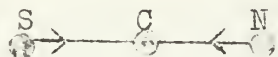
good single crystals for analysis. Schäffer (13) has suggested that it is possible to differentiate between a thiocyanate and an isothiocyanate structure on the basis of the position of the ligand in the spectrochemical series, to wit, $\text{Cl} \sim -\text{SCN} < \text{F} < \text{H}_2\text{O} < -\text{NCS} < \text{NH}_3 < \text{CN}$.

The use of infrared spectra offers the most convenient means of differentiating among the three types of thiocyanate bonding. The three fundamental vibratory modes of the thiocyanate ion are shown in Figure 1 (14), along with the corresponding frequencies exhibited by the free ion (15), as in KCNS. (It should be noted that writing the thiocyanate ion as CNS is meant to indicate that it is "ionic", i.e., uncomplexed, or, if in a complex ion, that the nature of the bonding is unknown. Writing the ion as NCS or SCN is meant to indicate that the ion is coordinated through the first atom written.)

Figure 1

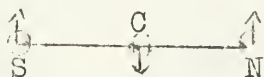
Fundamental Modes of Vibration of the Thiocyanate Ion

ν_1 : C-S Stretch (NCS symmetric)



$\nu_1 = 749 \text{ cm.}^{-1}$ for solid KCNS

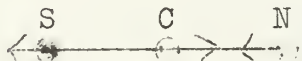
ν_2 : NCS Bending (doubly degenerate)



$\nu_{2a} = 484 \text{ cm.}^{-1}$ for solid KCNS

$\nu_{2b} = 470 \text{ cm.}^{-1}$ " " "

ν_3 : C-N Stretch (NCS anti-symmetric)



$\nu_3 = 2053 \text{ cm.}^{-1}$ for solid KCNS

All three frequencies are shifted upon complexation, the direction and/or magnitudes of the shifts varying with the mode of bonding.

Lewis, et al. (16), showed that the bending frequencies show a difference in trend between M-NCS and M-SCN complexes. The former have a band or bands of medium intensity lying near 470 cm.^{-1} , while the latter show, first, a shift to lower values and intensities and, secondly, a wider separation and greater number of frequencies.

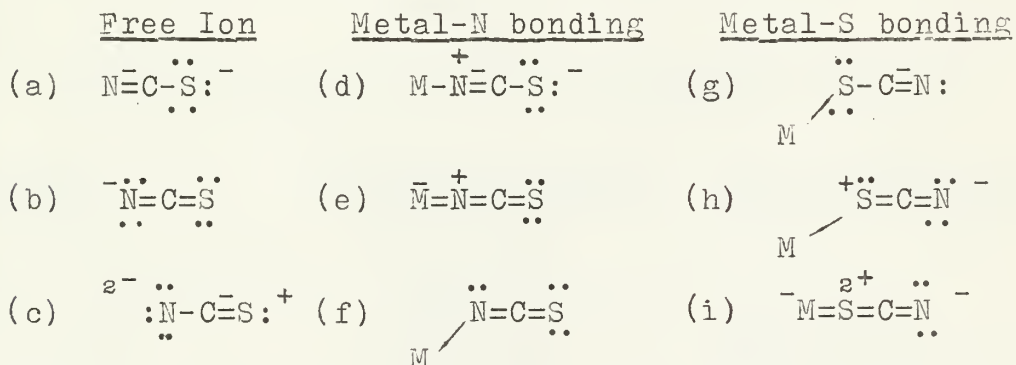
Mitchell and Williams (9) carried out a detailed study of the C-N stretching frequencies of complex thiocyanates. They came to the conclusion that the frequency is at higher wave numbers in the order $\text{CNS} < \text{M-NCS} < \text{M-SCN} < \text{M-SCN-M}$, all other factors remaining constant. Chatt and Duncanson (7) have pointed out that bridging thiocyanates in platinum(II) and palladium (II) complexes exhibit C-N stretching frequencies $> 2150 \text{ cm.}^{-1}$.

The most useful frequency is that of the C-S stretching mode. As first pointed out by Chamberlain and Bailar (17) and later, in greater detail, by Turco and Pecile (18), this frequency is shifted to higher wavenumbers in the spectra of isothiocyanates, and to lower wavenumbers in the spectra of thiocyanates, both relative to the C-S stretching frequency of KCNS. Turco and Pecile give the following ranges: M-NCS, $780\text{--}860 \text{ cm.}^{-1}$; M-SCN, $690\text{--}720 \text{ cm.}^{-1}$. In all cases studied thus far, the infrared results have invariably agreed with available X-ray crystallographic data.

The reason for the observed shifts may be seen by examining the canonical resonance structures (16) shown for free and complexed thiocyanate in Figure 2.

Figure 2

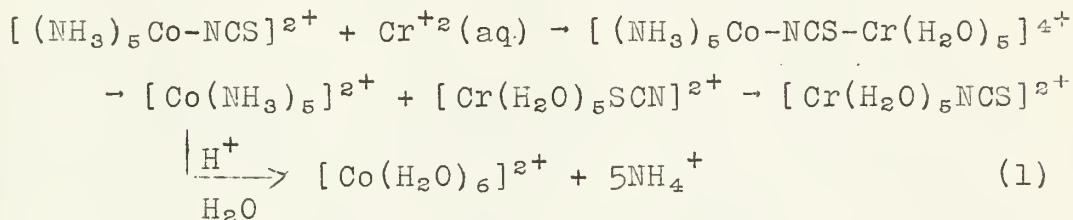
Canonical Resonance Structures



Jones (15) has calculated that, for the free ion, form (a) predominates (71%). X-ray results imply that, for S-bonding, only form (g) is important, while for N-bonding forms (f) or (d) occur. There is therefore a decrease in the C-S bond order when the thiocyanate becomes S-bonded, and an increase in the C-S bond order when the thiocyanate becomes N-bonded.

III. PREVIOUS ATTEMPTS TO PREPARE THIOCYANATE LINKAGE ISOMERS

The only previously reported attempt to prepare inorganic linkage isomers of the thiocyanate ion was for chromium(III) complexes, and was not successful (19). Carlin and Edwards' approach employed the reduction of $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ by chromium (II):



The reaction, which had been shown by Taube (20) to pass through an activated bridge intermediate, yielded only the stable chromium(III) N-bonded species, apparently because of a very rapid rearrangement of the chromium(III) S-bonded kinetic product.

The initial attempts to prepare thiocyanate linkage isomers in this study were formulated along the same lines, using $[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ as the oxidants and chromium(II) as the reductant and were also unsuccessful.

IV. EFFECTS OF OTHER LIGANDS ON THIOCYANATE BONDING

The realization of success in this study was made possible, to a large extent, by an interesting and significant observation made by Turco and Pecile (18), which is summarized in Table 1.

Table 1

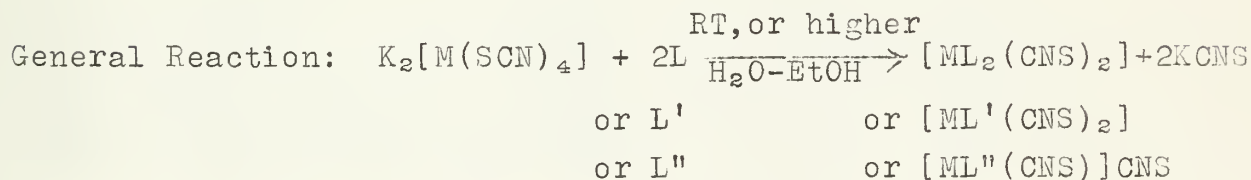
Effect of Other Ligands on Thiocyanate Bonding

Compound	C-N Stretch, cm^{-1}	C-S Stretch, cm^{-1}
$\text{K}_2[\text{Pd}(\text{SCN})_4]$	2118, 2086	703, 707(sh), 696(sh)
<u>trans</u> - $[\text{Pd}(\text{NH}_3)_2(\text{SCN})_2]$	2116, 2100	701
$[\text{Pd}(\text{PEt}_3)_2(\text{NCS})_2]$	2089	846, 842(sh)
$\text{K}_2[\text{Pt}(\text{SCN})_4]$	2120, 2089	697, 700(sh), 690(sh)
<u>cis</u> - $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$	2116	703
$[\text{Pt}(\text{PEt}_3)_2(\text{NCS})_2]$	2113	855

They found that, for Pd(II) and Pt(II) complexes, coordinated thiocyanate is either S- or N-bonded (S-bonding being the normal mode) depending on the nature of the other ligands present. Thus, the systems $[M(SCN)_4]^{2-}$ and $[M(NH_3)_2(SCN)_2]$ are S-bonded, whereas $[M(PR_3)_2(NCS)_2]$ is N-bonded. They point out that there are two sets of antibonding π -orbitals localized on the sulfur atom which, along with the sulfur atom's vacant d-orbitals, can accept t_{2g} electron density from the metal atom, resulting in additional stability of the M-S bond. The importance of this additional stability will depend on the availability of the t_{2g} electrons of the metal and their relative energy as compared with that of the orbitals of the thiocyanate. Strong π -electron acceptors, such as trialkylphosphines are believed to be, can make the t_{2g} electrons of the metal less available for donation to the thiocyanate, removing the source of additional stability for the M-S bond. It follows that, in these systems, there should be some borderline ligands for which the energy difference between the M-SCN and M-NCS isomers is relatively small, permitting isolation of both. Accordingly, the effects of a large number of ligands on thiocyanate bonding were studied, and the results are summarized in Table 2.

Table 2

Effect of Other Ligands on Thiocyanate Bonding



where M = Pd(II) or Pt(II)

L = monodentate ligand (Pd(II) complexes trans-, Pt(II) complexes cis-)

L' = bidentate ligand

L'' = tridentate ligand

Isothiocyanates

<u>Complex</u>	<u>C-N Stretch (cm.⁻¹)</u>	<u>C-S Stretch (cm.⁻¹)</u>
$[Pd(PBu_3^n)_2(NCS)_2]$	2102	847
$[Pd(PPh_3)_2(NCS)_2]$	2093	853
$[Pt(PPh_3)_2(NCS)_2]$	2097	859
$[Pd(AsBu_3^n)_2(NCS)_2]$	2111	844

Table 2 (Continued)

[Pd(AsPh ₃) ₂ (NCS) ₂]	2089	854
[Pt(AsPh ₃) ₂ (NCS) ₂]	2090	861
[Pd(py) ₂ (NCS) ₂]	2115	865
[Pt(py) ₂ (NCS) ₂]	2123	847
[Pd(bipy)(NCS) ₂]	2100	849, 842
[Pt(bipy)(NCS) ₂]	2095	854
[Pd(tripy)(NCS) ₂](bidentate)	2088	848
[Pt(tripy)NCS]CNS (tridentate)	2089, 2040	863

Thiocyanates

<u>Complex</u>	<u>C-N Stretch(cm.⁻¹)</u>	<u>C-S Stretch(cm.⁻¹)</u>
[Pd(SbPh ₃) ₂ (SCN) ₂]	2119(sh), 2115	*
[Pt(SbPh ₃) ₂ (SCN) ₂]	2123(sh), 2120	*
[Pd(γ-pic) ₂ (SCN) ₂]	2109	702
[Pd(4-n-ampy) ₂ (SCN) ₂]	2111	707
[Pd(o-phen)(SCN) ₂]	2114	696
[Pd(tu) ₂ (SCN) ₂]	2107	703
[Pd(etu) ₂ (SCN) ₂]	2101	701
[Pt(en)(SCN) ₂]	2114	696
<u>cis</u> -[Pt(NH ₃) ₂ (SCN) ₂]	2116	698
<u>trans</u> -[Pt(NH ₃) ₂ (SCN) ₂]	not det.	706

*No C-S stretching peak in N-bonded range; strong phenyl ring absorption in S-bonded range.

Abbreviations: py = pyridine
bipy = 2,2'-bipyridine
tripy = 2,2',2"-tripyridine
γ-pic = γ-picoline = 4-methylpyridine
4-n-ampy = 4-n-ampylpyridine
o-phen = o-phenanthroline
tu = thiourea
etu = ethylenethiourea

In each case, the analogous chloro complex was also prepared, in order to determine the position of the thiocyanate C-S stretching frequency by comparing the infrared spectra of both derivatives.

Further support for the π -bonding hypothesis of Turco and Pecile may be seen in the following observations:

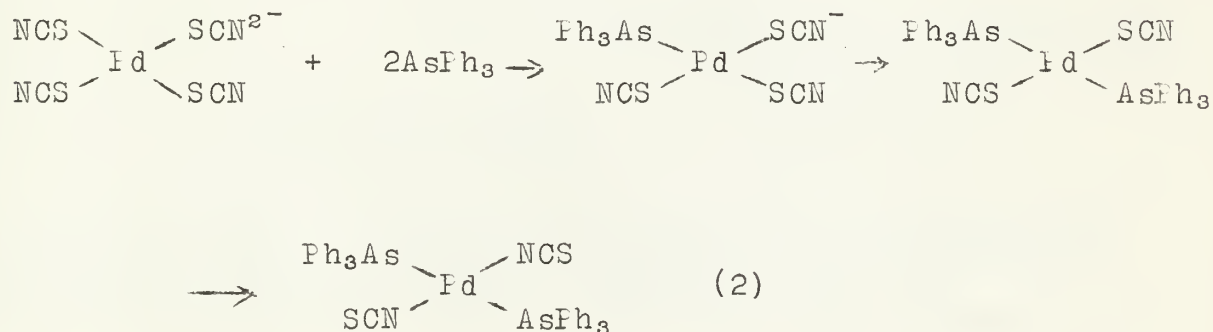
a) Considering the PPh_3 , AsPh_3 and SbPh_3 derivatives, a change from N- to S-bonded thiocyanates occurs in the SbPh_3 complexes. In the same order, the vacant d-orbitals of the donor atom are increasing in size and in energy, the capability of effective π -bonding with the metal atom presumably decreasing concurrently.

b) Comparing cis- $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$ with trans- $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$, one finds a lower C-S stretching frequency (698 cm^{-1}) in the spectrum of the former than that found in the spectrum of the latter isomer (706 cm^{-1}). This would correlate with a greater weakening of the C-S bond in the cis-isomer as a result of greater π -bonding from the metal atom. In the cis-isomer, each thiocyanate would have a filled metal d-orbital from which it could withdraw electron density, e.g., the d_{xz} and d_{yz} orbitals, whereas, in the trans-isomer, both thiocyanates would be sharing the same orbitals.

c) A change from Pd-NCS to Pd-SCN bonding occurs in going from the pyridine to the γ -picoline and 4-n-ampylpyridine derivatives. In the case of the latter complexes, the inductive and resonance (by virtue of hyperconjugation) effects of the alkyl groups both tend to donate electron density into the pyridine ring, opposing the withdrawal of d-electron density by the ring from the palladium.

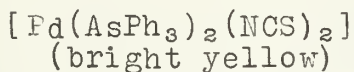
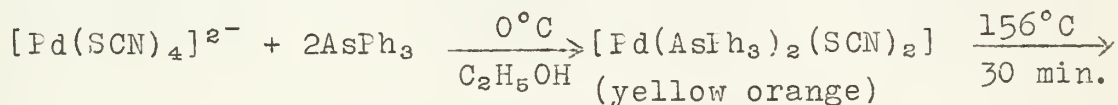
V. SYNTHESIS OF $[\text{Pd}(\text{AsPh}_3)_2(\text{SCN})_2]$ AND $[\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2]$

If one considers the reactions, at room temperature, leading to the formation of $[\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2]$,



the conclusion is reached that, after the substitution of the second AsPh_3 for the trans-labilized-SCN, the remaining two thiocyanates probably remain S-bonded for a short, but finite length of time before isomerizing to the evidently more stable N-bonded isomer. Hence, lowering the temperature of the reaction offers the possibility of isolating the S-bonded isomer. It is logical to predict that this system would offer the best opportunity for such isolation, since it lies between the extremes of the N-bonded IPh_3 and S-bonded SbPh_3 derivatives.

When the reaction was carried out in ethyl alcohol at 0°C ., a yellow-orange product was isolated (by precipitation with ice water) whose infrared spectrum showed the C-S stretching peak at 854 cm^{-1} , found in the spectrum of the N-bonded isomer, to be completely absent. As predicted by Mitchell and Williams (9), the C-N stretching peak was found at a higher frequency, 2119 cm^{-1} , than that (2089 cm^{-1}) of the N-bonded isomer. Heating the S-bonded isomer at 156°C for 30 minutes resulted in complete isomerization to the bright yellow N-bonded isomer. It was later determined, by the use of high resolution infrared spectroscopy, that what results from the reaction at room temperature is actually a mixture of the two isomers. The preparation and spectra of the isomers may be summarized as follows:



Infrared Spectra

	C-N Stretch(cm^{-1})	C-S Stretch(cm^{-1})
$[\text{Pd}(\text{AsPh}_3)_2(\text{SCN})_2]$	2119	obscured by Ph absorption
$[\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2]$	2089	854

Visible Transmission Spectra(Nujol mulls)

Transmission Minima(m μ)

$[\text{Pd}(\text{AsPh}_3)_2(\text{SCN})_2]$	395; 475(sh)
$[\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2]$	351

In c.a. 10^{-4} M chloroform solution, the visible spectra of the two isomers are identical, only the peak at $351\text{ m}\mu$ ($\epsilon = 2.09 \times 10^4$) being present, indicating an S \rightarrow N-bonded isomerization of the S-bonded isomer upon dissolution.

The molar conductances of the isomers, determined in dimethylformamide at 25°C., clearly show that they are both non-ionic complexes (Table 3).

Table 3

Molar Conductances in Dimethylformamide at 25°C.*

Compound	Concentration λ_{M} (mho cm. ⁻² mole ⁻¹)	
[Pd(AsPh ₃) ₂ (SCN) ₂]	1.00 x 10 ⁻³ M	13.3
[Pd(AsPh ₃) ₂ (NCS) ₂]	"	13.8
[Pd(AsPh ₃) ₂ Cl ₂]	"	8.5
[Ph ₄ As]Cl	"	64.3
[Bu ₄ ⁿ N]I	"	75.8
Na[BPh ₄]	"	55.7
[Ph ₄ As][BPh ₄]	"	45.5
[Zn(INO) ₂ Cl ₂]	2.91 x 10 ⁻³	7.0(ref. 21)
[Cu(FNO) ₂ Cl ₂]	2.02 x 10 ⁻³	15.9(" ")
[Sn(FNO) ₂ Br ₄]	0.99 x 10 ⁻³	23.9(" ")

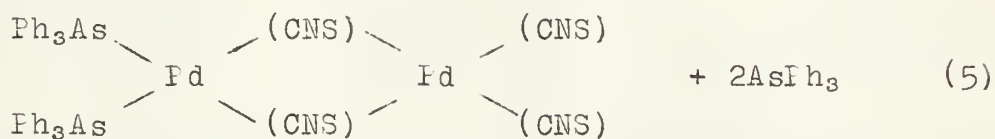
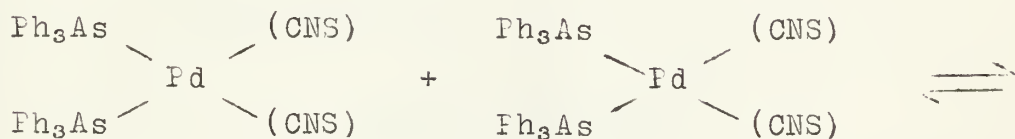
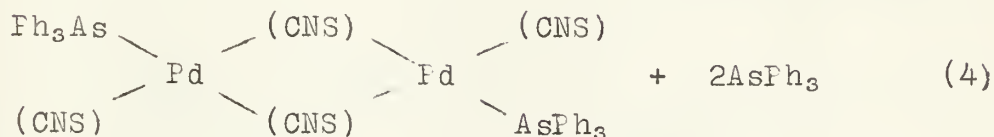
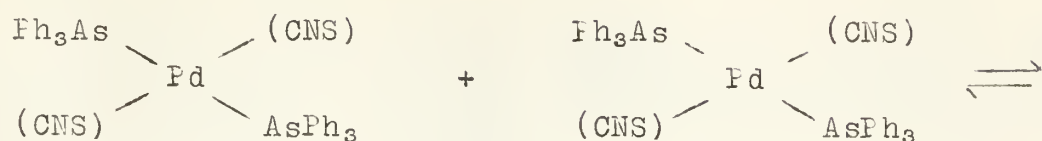
FNO = pyridine N-oxide

*In general, Quagliano, et al. (21), give the following conductance ranges for complexes in DMF at 25°C:

1:1 downward from 85
 2:1 140-170
 3:1 200-260

To disprove the possibility of concurrent geometric isomerism, i.e., trans-S-bonded - cis-N-bonded, or vice-versa, the dipole moments of both isomers were determined in benzene (conc. $\approx 10^{-2}$ M). The results were inconclusive. The dipole moment of the S-bonded isomer was found to be 3.87 D., that of the N-bonded isomer 3.58 D. However, the infrared spectra in the C-N stretching range of the benzene solutions used in the determinations proved to be identical, both showing three C-N stretching peaks: the N-bonded C-N stretch at 2089 cm.⁻¹, the S-bonded C-N stretch at 2119 cm.⁻¹, and a peak at 2160 cm.⁻¹, attributable to bridging, which could take place by either of the following

reactions, depending upon whether the initial complex is cis- or trans-:

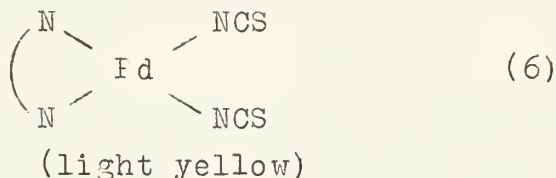
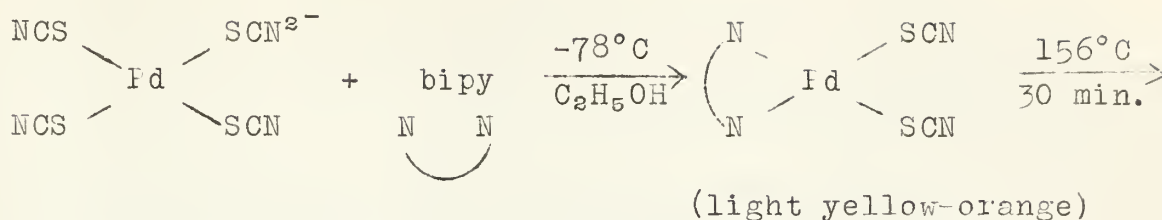


Further evidence for bridging was found in the decrease in intensity of the 2160 cm.^{-1} peak resulting from the addition of some free AsPh_3 , which would shift the equilibrium to the left. The 2089 cm.^{-1} peak increased in intensity concurrently. X-ray powder patterns of the two isomers showed them to be non-isomorphous.

VI. SYNTHESIS OF $[\text{Pd}(\text{bipy})(\text{SCN})_2]$ AND $[\text{Pd}(\text{bipy})(\text{NCS})_2]$

To obviate the possibility of concurrent geometric isomerism, it was decided that a bidentate ligand should be employed in a similar fashion as was the triphenylarsine, since only the cis-configuration would be possible for both isomers. Bipyridine was the ligand of choice. As shown in Table 2, the product, at room temperature, of the reaction between $[\text{Pd}(\text{SCN})_4]^{2-}$ and bipyridine was light yellow $[\text{Pd}(\text{bipy})(\text{NCS})_2]$. Isolation of the light yellow orange S-bonded isomer was accomplished by lowering the temperature of the reaction to -78°C (the temperature of a

Dry Ice-acetone bath):



Infrared Spectra

	C-N Stretch, cm. ⁻¹	C-S Stretch, cm. ⁻¹
[Pd(bipy)(SCN) ₂]	2117, 2108	700
[Pd(bipy)(NCS) ₂]	2100	849, 842

The molar conductances of both isomers showed them to be non-ionic (Table 4).

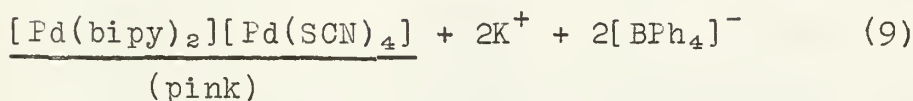
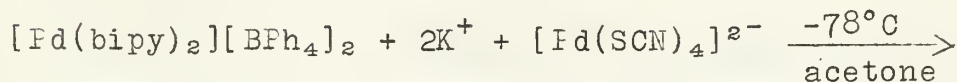
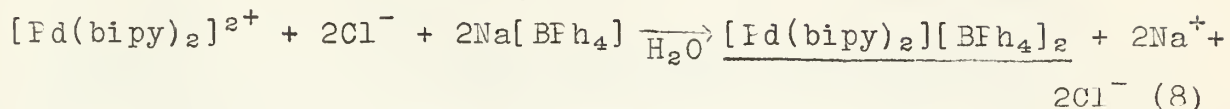
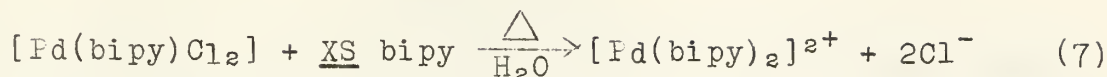
Table 4

Molar Conductances in Dimethylformamide at 25°C.

Compound	Concentration	Λ_M (mho cm. ² mole ⁻¹)
[Pd(bipy)(SCN) ₂]	1.00 x 10 ⁻³ M	20.3
[Pd(bipy)(NCS) ₂]	"	20.8
[Pd(bipy)Cl ₂]	"	9.4
[Pt(bipy)Cl ₂]	"	5.0
[Pd(bipy) ₂](ClO ₄) ₂	"	143

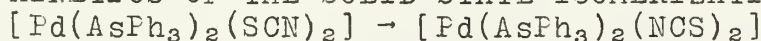
The only other possible compound which would give the same analytical results and possibly the same infrared spectrum as the S-bonded isomer is [Pd(bipy)₂][Pd(SCN)₄]. Although the conductivity measurements seem to rule out this possibility, it was felt that the most convincing evidence would be gained by actually preparing the Magnus' type salt. After much trial and error, the following procedure

was successfully employed:



The visible transmission spectrum of a Nujol mull of the product exhibited the shoulders at 500 and 410 m μ which are also found in the spectrum of $\text{K}_2[\text{Pd}(\text{SCN})_4]$.

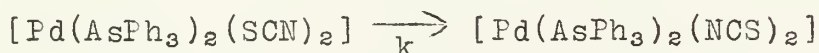
VII. KINETICS OF THE SOLID STATE ISOMERIZATION



The kinetics of the above isomerization were followed by observing the decrease in intensity of the S-bonded C-N stretching peak at 2119 cm^{-1} as a function of time. The isomerizations were carried out in potassium bromide disks heated to the desired temperature. The high pressure encountered in the preparation of the disks caused partial isomerization to occur, but this did not cause any difficulty in carrying out the measurements. It would have been desirable to follow the isomerizations in heated Nujol mulls, but the high temperatures employed resulted in experimental difficulties which prohibited this. The rate constants obtained are shown in Table 5.

Table 5

Rates of Isomerization of $[\text{Pd}(\text{AsPh}_3)_2(\text{SCN})_2]$
in the Solid State



t(°C)	k x 10 ⁵ (sec. ⁻¹)	t _{1/2} (hr.)	Medium
126	3.47	5.55	KBr disk
145	7.81	3.10	" "

Qualitatively, it was observed that, in the pure solid state, complete isomerization took place in less than two hours at 118°C. The rate constants shown above, therefore, do not represent the true rates of isomerization and, hence, no other kinetic runs were made using the KBr disk technique and no thermodynamic parameters were calculated.

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CARBORANES

A NEW SERIES OF ORGANOBORANES

George Hartwell

December 10, 1963

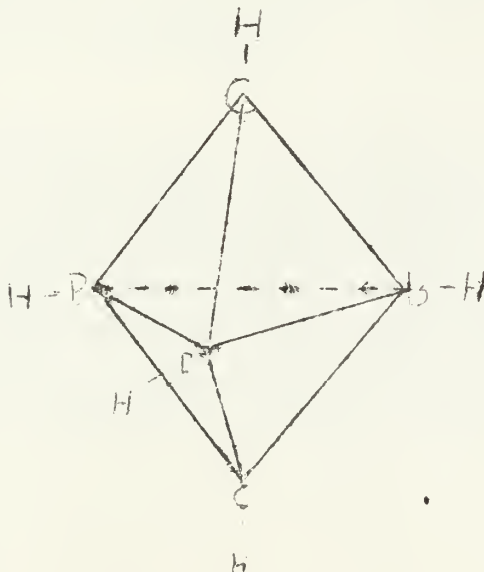
INTRODUCTION

In addition to the well known boron hydride series, many organoboron compounds containing the carbon-boron bond have been investigated, and the chemistry of organo-boron derivatives is becoming as complex and varied as that of carbon compounds.

One of the newest facets of boron chemistry is the carborane series, $B_nC_2H_{n+2}$, containing the carbon-boron bond without any B-H-B hydrogen bridge bonds. The series of compounds was first realized in a silent discharge reaction in 1953, although not announced until late in 1961 (1). At present the literature available about these compounds includes speculation as to the bonding and structure of the carboranes, with specific articles covering $B_3C_2H_5$ and $B_4C_2H_6$, the simplest compounds. A more extensive investigation has been made into the chemistry of carborane, $B_{10}C_2H_{12}$ and will be published shortly (11-16).

 $B_3C_2H_5$

The simplest member of the carborane family, $B_3C_2H_5$, was recovered in small yields from the reaction of pentaborane and acetylene (1) along with $B_4C_2H_6$ (two isomeric forms) and $B_5C_2H_7$. By the use of mass spectra, NMR, and infra red spectroscopy, the small amount of product melting at -126.4°C and boiling at -3.7°C was assigned a trigonal bipyramid configuration; no isomer of this compound was detected:

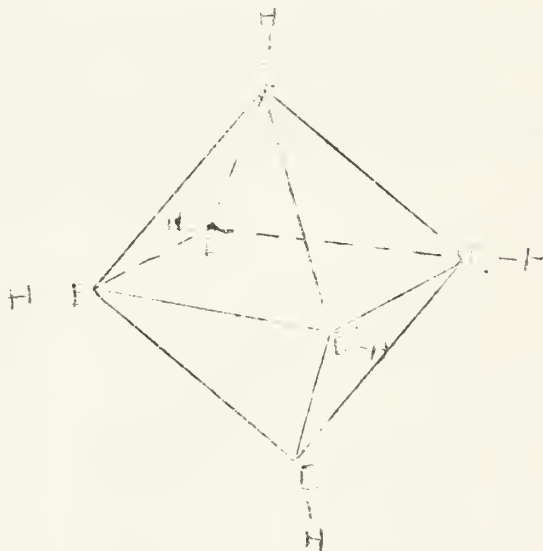
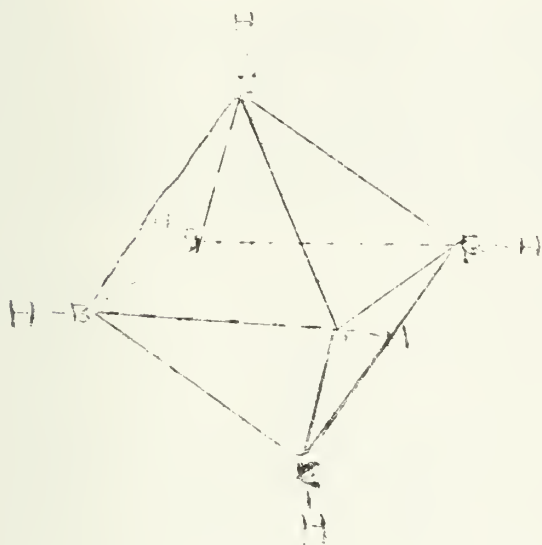


carborane-3

At room temperature the compound is very stable, even in contact with CO_2 , air, and water. No decomposition was noted over an extended period.

$\text{B}_4\text{C}_2\text{H}_6$

The next compound of the family is $\text{B}_4\text{C}_2\text{H}_6$, or carborane-4, produced in the same manner as carborane-3 (2). Using the same physical methods the structures of two isomers were proposed as octahedra:



sym-carborane-4

M.P. -32.6

B.P. 22.7

unsym-carborane-4

The same degree of high stability was observed for these isomers as for carborane-3.

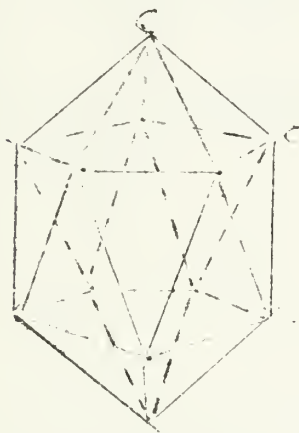
DISCUSSION

Previous molecular orbital calculations for $\text{B}_5\text{H}_6^{2-}$ and $\text{B}_6\text{H}_6^{2-}$ (3-6, 17) indicated the probable stability of these anions and the possibility of carbon atom substitution for B, thereby producing the isoelectronic neutral carborane series. Hoffmann and Lipscomb (6) have calculated the probable reactivities for carboranes and the most stable isomers, and recently (7) have proposed a mechanism for intramolecular rearrangements after the addition of an acetylenic group to the boron hydride polyhedron.

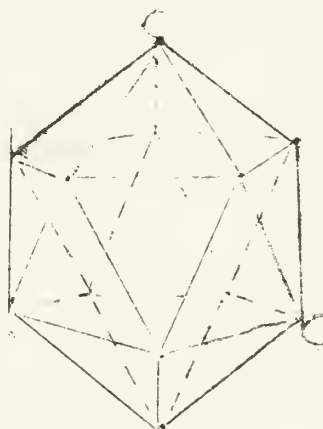
$B_{10}C_2H_{12}$

As previously mentioned, $B_{10}C_2H_{12}$, carborane-12, or more commonly "carborane" has received much attention, undoubtedly because it can be produced easily in fairly large yields. It was first observed in the reaction of bis(acetonitrile) decaborane with acetylene in refluxing benzene (13). Previous to that time, the anion $B_{12}H_{12}^{2-}$ had been proposed (8), prepared (9), its structure determined (10) and an MO bonding description presented (4).

The icosahedral structure for the $B_{12}H_{12}^{2-}$ ion requires 26 bonding electrons, the decaborane nucleus contributing 24 and the other two present because of the double negative charge on the anion; a neutral species was thereby precluded. Hoffmann and Lipscomb (6,7) predicted an icosahedral carborane from the reaction of decaborane and acetylene, and this compound was produced in two isomeric forms:



carborane (ortho)



iso-carborane (meta)

The meta isomer is the more stable, as was predicted from bonding principles (5) and MO theory (6).

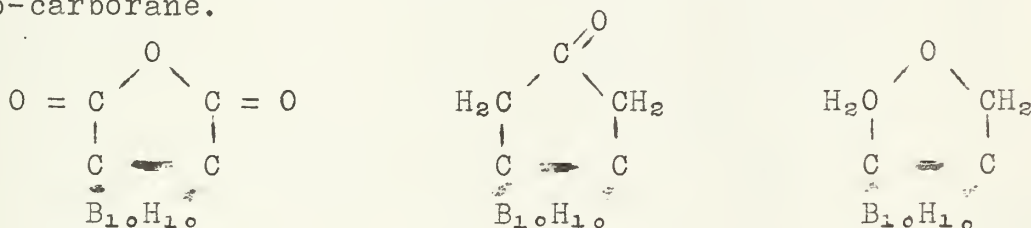
REACTIONS OF $B_{10}C_2H_{12}$

As part of the further investigation of carborane, its direct chlorination was studied (12). The stepwise chlorination was easily followed giving compounds from two to eleven chlorine atoms per molecule, with isomers for $B_{10}H_8Cl_2C_2H_2$ and $B_{10}H_6Cl_4C_2H_2$. Only $B_{10}H_3Cl_7C_2H_2$ seems to lack existence, although $B_{10}H_5Cl_5C_2H_2$ and $B_{10}HCl_9C_2H_2$ were present only as minor impurities. Of interest is the manner in which those compounds with greater than six chlorine atoms can be titrated as "carbon-acids" and the corresponding salts of neutralization isolated.

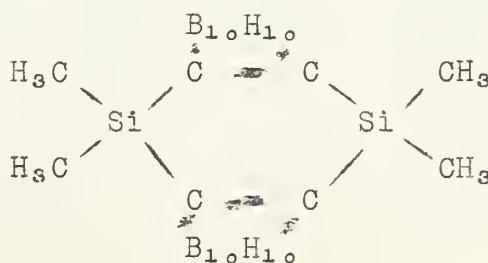
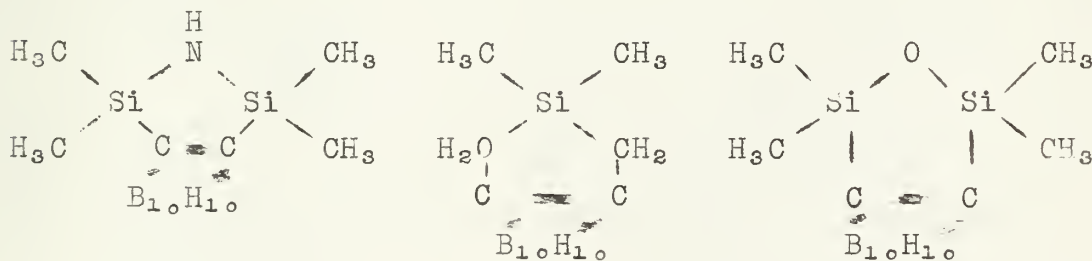
The ease with which acetylene combined with decaborane in mild Lewis bases as solvents lead to direct reactions between substituted acetylenes and decaborane yielding a great variety of compounds (see Table I) (13).

Carborane was found to react readily with a variety of organo-metallic compounds to produce mono and di-substituted derivatives which in turn undergo many reactions common to organometallics. Thus the icosahedron has been involved in many common reactions (14).

Outstanding among the various reactions was the production of a five-membered ring systems involving the ortho-carborane.



Metallo carboranes were also useful in synthesizing several silylcarboranes and corresponding ring systems, for example: (14 and 15)



Later (16) phosphorous was also included in carborane structures and ring systems:

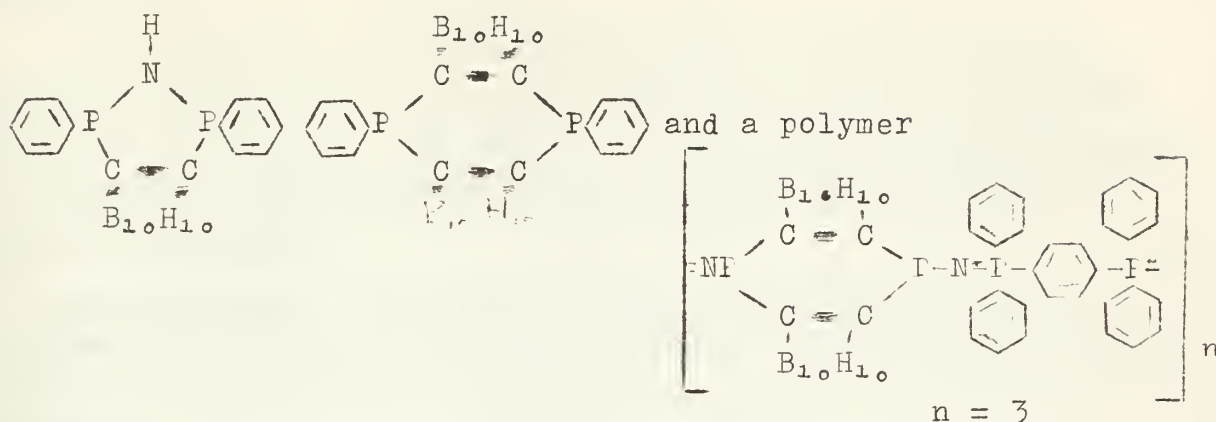


Table I
Substituted Carboranes
Prepared by Direct Synthesis

R - C - C - R'		Yield, %	M.P., °C	B.P., °C
R	R'			
1	H	65-77	320	--
2	-CH ₃	--	114-115	--
3	-CH=CH ₂	65-70	78-79	--
4	-CH ₃ -C-CH ₂	70	45-46	--
5	n-C ₃ H ₇	--	62	--
6	n-C ₄ H ₉	--	--	75/0.01
7	-(CH ₂) ₂ CH(CH ₃) ₂	23	33	--
8	-C ₆ H ₅	27	66-67	--
9	n-C ₆ H ₁₃	--	--	101-2/0.5
10	-(CH ₂) ₃ -C≡C-H B ₁₀ H ₁₀	--	355-357	--
11	-CH ₂ Br	70	30	--
12	-COOCH ₃	35	73	--
13	-CH ₂ Cl	74	119-120	--
14	-CH ₂ OOCCCH ₃	83	42-43	--
15	-n-C ₃ H ₇	66	44-45	107/1
16	-n-C ₄ H ₉	37	--	85-90/.5
17	-(CH ₂) ₂ OOCCCH ₃	72	61-63	146/1.6
18	-CH(OOCCCH ₃)CH ₃	66	--	85-95/0.2
19	-CH ₂ N(C ₂ H ₅) ₂	ca50	33-35	--
20	-CH ₂ OOCCCH ₃ -CH ₂ OOCCCH ₃	89	43-44	--
21	-COOCH ₃	54	66-67	--

CONCLUSION

A novel series of boron-carbon compounds has attracted attention, having previously been predicted and only recently isolated and studied. The interesting and great variety of reactions of carborane has produced a wide field of investigation and leaves the smaller members of the carboranes untouched in the search for compounds of the same nature; which have a predicted reactivity.

Bonding theory and synthesis have gone hand in hand in the founding of the family of carboranes. Further developments should follow quickly.

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The series of papers to be published are scheduled to appear in Inorganic Chemistry 1963-64. I wish to thank T. L. Heying of Olin Research Center for preprints of these papers.

LOW TEMPERATURE MAGNETIC SUSCEPTIBILITY STUDIES OF SOME COPPER(II) COMPOUNDS

George S. McArthur

December 17, 1963

I. INTRODUCTION

Magnetic susceptibility measurements have been used for many years in inorganic chemistry. Their use is usually limited to a single measurement at room temperature. The effective magnetic moment, μ_{eff} , is obtained from the observed susceptibilities according to the Curie formula

$$\chi = \frac{N \mu_{\text{eff}}^2}{3 kT}.$$

In the "spin only" case, where only the spin angular momentum of the electrons contributes to the magnetic moment, the number of unpaired electrons is calculated from the equation

$$\mu_{\text{eff}} = [n(n+2)]^{1/2} \text{ B.M.}$$

However, in order to calculate g values and spin-spin coupling constants, it is necessary to measure susceptibilities over a wide temperature range.

II. COPPER HALIDES

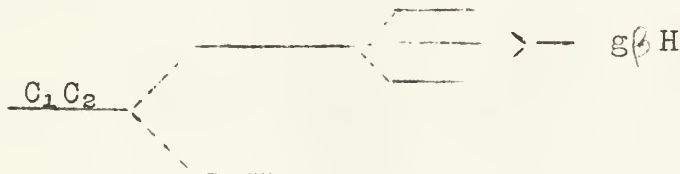
The compound $\text{CuX}_2 \cdot 2\text{H}_2\text{O}$ is a good example of antiferromagnetic substances whose behaviors agree with the theories of Néel, Van Vleck, and Anderson. Since these theories were discussed recently in this seminar (1), we shall merely review them briefly. In these substances there are two sublattices with electron spins oriented oppositely.

A single crystal of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ shows the spontaneous magnetization oriented along the a axis. The Néel temperature is 4.33°K . (2) For powdered $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ the peak in the susceptibility curve is at 5.2°K while the a -axis susceptibility peak in the crystal is at 4.8°K . (3) CuCl_2 and CuBr_2 , also are antiferromagnetic. A higher temperature (4), showing that as delocalization of the electrons increases, the interaction between sublattices also increases, is exhibited by the bromide as compared with the chloride.

III. COPPER ACETATE HYDRATE

The magnetic susceptibility of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ is unusually low. At room temperature $\mu = 1.38$ B.M. The susceptibility decreases rapidly with temperature and goes to zero at about 75°K . (5)

The ground state for the d^9 Cu^{2+} ion is $^2D_{5/2}$. It has been suggested that isolated pairs of Cu^{2+} ions interact strongly through exchange forces, each pair forming a lower singlet and an upper triplet state. Only the latter is paramagnetic. The crystalline field acting on each copper ion is similar to that in other salts (6).



Using this approach the lowest energy state may be denoted C_1C_2 since its wave function is the product of the individual wave functions for copper ions 1 and 2 in the pair. The fourfold degeneracy is partly removed by exchange interaction, which splits the level into a singlet and a triplet level. The applied magnetic field splits the triplet level. As the temperature is raised above 0°K , the triplet level is populated at the expense of the singlet. Therefore the susceptibility increases rapidly until a maximum is reached. Above this temperature the susceptibility decreases with increasing temperature (7).

The exchange interaction between two Cu^{2+} ions is expressed as $-JS_1S_2$ ($J < 0$). For a Cu^{2+} ion, the anisotropic field may be neglected and we may write:

$$\mathcal{H} = J\vec{S}_1\vec{S}_2 + g\beta SH$$

$$S = \vec{S}_1 + \vec{S}_2$$

Therefore, $2 S_1S_2 = S(S+1) - S_1(S_1+1) - S_2(S_2+1)$

$$\mathcal{H} = 1/2 JS(S+1) + g\beta SH$$

The magnetic susceptibility can then be shown to be

$$\chi_m = \frac{Ng^2\beta^2}{kT} \frac{\exp(-J/kT)}{1 + 3\exp(-J/kT)}$$

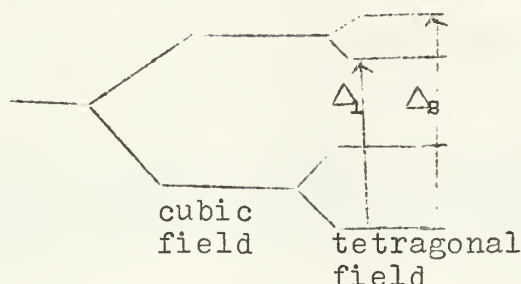
Without including the temperature independent paramagnetism (8).

For a Cu^{2+} ion in a tetragonal field it can be shown that (9)

$$g_{||} = 2 \left(1 - \frac{4\lambda}{\Delta_1} \right)$$

$$g_{\perp} = 2 \left(1 - \frac{\lambda}{\Delta_2} \right)$$

taking $\lambda = 828 \text{ cm}^{-1}$.



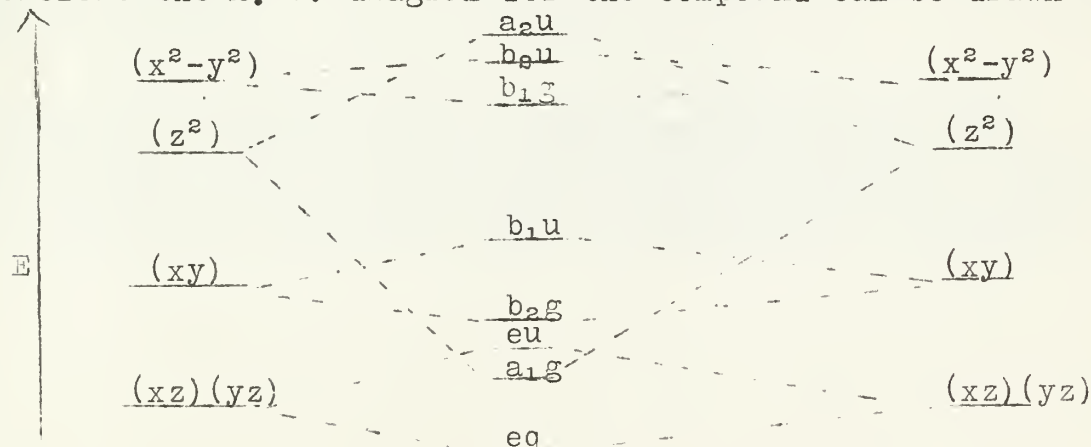
It is found that $\Delta_1 = 15,000 \text{ cm}^{-1}$

$$\Delta_2 = 20,700 \text{ cm}^{-1} \quad (8).$$

The structure of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ has been found to be dimeric, with a water molecule bonded to each metal ion, and with four bridging acetate groups.

J has been found as $430 \pm 15^\circ \text{K}$. This could hardly be expected without direct coupling (8). The hole in the Cu^{2+} ion would be expected to be in the $d_{x^2-y^2}$ orbital since the lobes are in the direction of the negative ligands. Therefore σ bonds are predicted. Although the d_{z^2} orbitals would have a larger overlap than the $d_{x^2-y^2}$ orbitals the difference is not large enough to favor electron promotion for σ bonding (7).

Ballhausen in his studies has reached a different conclusion (22). If the dimer is considered as two separate units, each will belong to the C_{4v} point group. The dimer will belong to the D_{4h} point group. The energy levels in $\text{CuO}_4 \cdot \text{H}_2\text{O}$ would be expected to resemble those in $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. Therefore the M. O. diagram for the compound can be drawn



The large splitting in the two d_{z^2} M.O.'s results from the large overlap.

The wavefunction for the complex can be written

$$\Psi(^1A_{1g}) = |(e_g)^4(a_{1g})^2(e_u)^4(b_{2g})^2(b_{1u})^2(b_{1g})^2(b_{2u})^2|$$

The first excited triplet will be

$$\Psi(^3B_{1g}) = |(e_g)^4(a_{1g})^2(e_u)^4(b_{2g})^2(b_{1u})^2(b_{1g})^2(b_{2u})^1(a_{2u})^1|$$

From the overlap criteria σ bond seems more likely and will suffice to account for the electronic features of the compound. The authors feel the possibility of "super exchange" thru the acetate groups is less probable.

IV. HYDRATES OF COPPER FORMATE

The room temperature susceptibility of $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ gives a result of $\mu = 1.64$ B.M. This is lower than the usual value of 1.9 B.M. for Cu^{2+} , but not as low as the value for copper acetate. The structure of the tetrahydrate is an open layer composed of elongated CuO_6 octahedra linked together in an infinite two-dimensional array. There are two water molecules in the octahedron, one lying above and the other below the CuO_4 plane. The CuO_4 planes do not lie in the plane of the Cu atoms. Adjacent octahedra are slightly rotated contrariwise to one another. The remaining two water molecules are not bonded directly to the copper ions, but are hydrogen bonded between adjacent layers which are 6.2 Å. apart (11).

Martin and Waterman studied this compound down to 80°K. They thought that the compound was antiferromagnetic with the Néel point slightly under 80°K. (11). Flippin and Friedberg (12), as well as Haseda (13), studied the susceptibility down to liquid helium temperatures. Both found a sharp peak at 16.8°K. This seems to indicate a weak ferromagnet. i.e., an antiferromagnet whose sublattice magnetizations are slightly canted.

Flippin and Friedberg found that the Cu^{2+} exchange coupling in $\text{Cu}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ is much weaker than in the tetrahydrate and probably qualitatively different. Although the structure of the dihydrate is unknown, this does seem to confirm the conclusion that the structure is different (12).

V. $\text{Cu}(\text{NH}_3)_5\text{H}_2\text{O SO}_4$

Authors agree that this compound has a maximum in the susceptibility curve at 3.4°K . Comparing Cu-Cu distances shows there cannot be direct interaction. However, there are long chains of Cu-H₂O-Cu which could account for the pairing of spins (14). The values for g at the Néel point are approximately equal (15). L. Bellomonte has suggested that the anisotropy in g values decreases when the temperature is lowered from 4 to 2°K . and increases between 2 and 1°K . This might indicate that the Cu-H₂O distance decreases from 4 to 2°K ., while at 2°K . magnetostriction sets in (16).

VI. CuSO_4 HYDRATES

At room temperature all the copper sulfate hydrates have $\mu = 1.94$ B.M., while for the anhydrous copper sulfate $\mu = 1.77$ B.M. (17). The anhydrous salt shows a sharp peak at 34.4°K . (18). Krienens has shown that the peak is in χ while χ' decreases regularly with temperature. This suggests an antiferromagnetic interaction similar to that proposed for copper formate tetrahydrate (19).

VII. $\text{Cu}(\text{AcAc})_3$

The maximum in the susceptibility curve for the trisacetylacetone complex of copper(II) is at 1.03°K . The authors speculate that a transition permits delocalization of unpaired d electrons between molecules, leading to a nearly degenerate ground state (20).

Eisenstein has derived the Hamiltonian for Cu-Cu spin orbit coupling. He shows that the exchange interaction completely dominates the dipole-dipole term in calculating the magnetic susceptibility (21).

VIII. CONCLUSIONS

When interpreting magnetic susceptibility, it must be remembered that this is a bulk property. The susceptibility found is a weighted mean of the individual magnetic susceptibilities of all the populated states of the molecule. Therefore, it is important that it be determined if the molecule is in its ground state or a randomly oriented temperature dependent excited state.

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2. The second part is devoted to a detailed study of the various theories of the subject.	2
3. The third part is devoted to a critical examination of the various theories of the subject.	3
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VIBRATIONAL SPECTRA AND BONDING IN METAL CARBONYLS

Richard S. Treptow

March 3, 1964

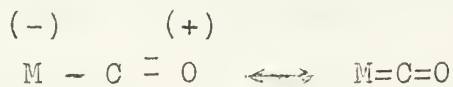
INTRODUCTION

Since their discovery seventy years ago, the carbonyl compounds of transition metals have had a position of unique interest for the coordination chemist. In contrast to the usual metal complexes, these substances are volatile, stabilize the central metal in low oxidation states, and are relatively stable in spite of the poor donor ability of carbon monoxide.

In this seminar only mononuclear, octahedral metal carbonyls and their derivatives will be discussed. This selection has been made owing to the large amount of infrared investigation currently being done on species of this type, and because their symmetry permits relatively simple theoretical discussion. A more general survey of various properties and structures has recently been published (1).

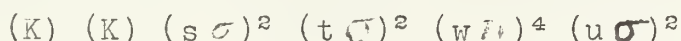
BONDING

Theories, while differing in approach to the problem, are nevertheless in general agreement as to the nature of bonding in these compounds. In the valence bond model the metal-carbonyl interaction is described by two resonance forms:



In the second canonical structure dative metal-carbon bonding reduces the excess negative charge on the metal in keeping with the electroneutrality principle.

In molecular orbital theory the ground state of carbon monoxide is represented:



with additional unfilled ($v\pi$) ($r\sigma$) orbitals (2). When this molecule is bonded to a metal atom, σ -bonding results from the interaction of the lone pair carbon orbital (the $(u\sigma)^2$, which is approximately an sp hybrid) and the metal $d_{x^2-y^2}$ and d_{z^2} orbitals (the e_g orbitals). There is also σ -bonding with the metal s and p orbitals. The most important π -interactions involve the $(w\pi)^4$ bonding and ($v\pi$) antibonding orbitals of carbon monoxide combined with the metal d_{xy} , d_{xz} and d_{yz} orbitals (the t_{2g} orbitals). Other interactions are of secondary importance. Energy level schemes have recently been advanced by H. B. Gray et. al. for $M(CO)_6$ (3) and $Mn(CO)_5X$ (4).

An important conclusion should be noted: In molecular orbital theory increased metal-to-carbon π -bonding puts more electron density into the π -antibonding orbital of CO, thus weakening that bond. The same conclusion concerning metal-carbon multiple bonding and CO bond strength may be derived from the two resonance forms of valence bond theory. The link between extent of metal π donation and CO stretching frequencies is thus established.

CARBONYL STRETCHING FREQUENCIES

The effect of overall charge on the species offers a simple test of the principle just explained. Consider the frequency shifts in the isoelectronic series of Table I.

Table I Effect of Charge on CO Stretching Frequencies (5,6,7)

$[V(CO)_6]^-$ 1859 cm^{-1}	$Cr(CO)_6$ 1986 cm^{-1}	$[Mn(CO)_6]^+$ 2090 cm^{-1}
	$Mo(CO)_6$ 1986	
	$W(CO)_6$ 1983	$[Re(CO)_6]^+$ 2082

The anionic complex shows the lowest frequency and should have, therefore, the largest amount of metal-carbon π -bonding. This is consistent with the principle that negative charge facilitates delocalization of the d electrons.

When one or more CO group is replaced by another ligand, the availability of d electrons to the remaining carbonyl groups is altered. Since 1959 a large amount of spectral data has been obtained on derivatives where the ligand introduced is halide (8-10), nitrile (11,12), isonitrile (13), various sulfur donors (14-16), oxygen donors (17,18) and phosphorus, arsenic, antimony and bismuth donors (19-25). Table II shows the effect various ligands have on the carbonyl frequencies.

Table II Bonding Effect of Other Ligands on
CO Stretching Frequencies in cis $L_3M(CO)_3$

<u>Donor Atom</u>	<u>Compound</u>	<u>CO Stretch</u>		<u>ref.</u>
		<u>A₁ mode</u>	<u>E mode</u>	
N	py ₃ Mo(CO) ₃	1888	1746	(20)
N	dien Cr(CO) ₃	1881	1735	(20)
N	dien Mo(CO) ₃	1883	1723	(20)
N	dien W(CO) ₃	1873	1718	(20)
P	(Ph ₃ F) ₃ Mo(CO) ₃	1949	1835	(20)
P	(Me ₃ F) ₃ Mo(CO) ₃	1944	1854	(19)
P	(Et ₃ F) ₃ Mo(CO) ₃	1937	1841	(19)
As	(Et ₃ As) ₃ Mo(CO) ₃	1938	1843	(15)
Sb	(Et ₃ Sb) ₃ Mo(CO) ₃	1944	1859	(21)

The CO bond order is clearly less in the cases of nitrogen donors. Because nitrogen does not have suitable orbitals there is no competition for the metal d π electrons. This is not the case with P, As, and Sb.

The extent to which a donor such as phosphorus acts as a π -acceptor is altered by the electronegativity of other groups bonded to the phosphorous. This effect is seen in the series of Table III (20).

Table III Inductive Effect of Other Ligands
on the CO Stretching Frequencies
in cis $(FX_3)_3 Mo(CO)_3$.

<u>Compound</u>	<u>CO Stretch</u>	
	<u>A₁ mode</u>	<u>E mode</u>
(Ph ₃ P) ₃ Mo(CO) ₃	1949	1835
(Ph ₂ PCl) ₃ Mo(CO) ₃	1977	1885
(PhFCl ₂) ₃ Mo(CO) ₃	2016	1943
(FCl ₃) ₃ Mo(CO) ₃	2041	1989

The attachment to phosphorous of an electronegative atom such as chlorine enhances the π -acceptor ability of the phosphorous.

A logical result of this type of work has been a ranking of ligands in the order of their π -acceptor ability. A recent and inclusive listing has been compiled by Horrocks and Taylor (26).

"SPECTROCHEMICAL SERIES" for π -Bonding Ligands













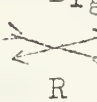
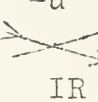




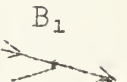
NO	As(OCH ₃) ₃	P(C ₆ H ₅) ₃
CO	P(Cl(OC ₄ H ₉)) ₂	S(C ₂ H ₅) ₂
PF ₃	As(OC ₂ H ₅) ₃	As(C ₂ H ₅) ₃
SbCl ₃	P(OC ₆ H ₅) ₃	P(CH ₃) ₃
AsCl ₃	P(Cl(C ₆ H ₅)) ₂	P(C ₂ H ₅) ₃
P(Cl ₃	p-Tolylisonitrile	o-C ₆ H ₄ [P(C ₂ H ₅) ₂] ₂
P(Cl ₂ (OC ₄ H ₉))	P(OC ₃ H ₇) ₃	P(NC ₅ H ₁₀) ₃
P(Cl ₂ (OC ₂ H ₅))	t-Butylisonitrile	o-Phenanthroline
P(Cl ₂ (C ₆ H ₅))	As (NC ₅ H ₁₀) ₃	Diethylenetriamine
PBr ₂ (CH ₃)	As (C ₆ H ₅) ₃	

There are dangers involved in making deductions such as these on the basis of frequency values from the literature. The spectra are not always easily compared due to differences in media and instrumentation (especially optics). Even when these effects are minimized, it is difficult to compare frequencies in molecules of different symmetry. Their modes of vibration are different so that a direct comparison of frequencies is not possible. In such cases deductions can be made only on the basis of force constants.

SYMMETRY, VIBRATIONAL MODES, AND BAND ASSIGNMENTS

The 3N-6 vibrational modes of a polyatomic molecule are infrared or Raman active according to selection rules, which depend upon the symmetry of the modes. Detailed descriptions of the group theoretical methods for determining normal modes are available in general works (27-29). For the compounds under discussion here the fundamental CO stretching modes (19,30) are shown in Table IV.

Table IV Carbonyl Stretching Modes

<u>Molecule</u>	<u>Symmetry</u>	<u>Mode and Activity</u>			
$M(CO)_6$	O_h	A_{1g}  R	E_g  R	T_{1u}  IR	
$M(CO)_5L$	C_{4v}	A_1^{1a}  IR and R	A_1^{1b}  IR and R	E  IR and R	B_1  R
<u>cis</u> - $M(CO)_4L_2$	C_{2v}	A_1^{1a}  all IR and R	A_1^{1b}  all IR and R	B_1  all IR and R	B_2  all IR and R
<u>trans</u> - $M(CO)_4L_2$	D_{4h}	A_{1g}  R	B_{1g}  R	E_u  IR	
<u>cis</u> - $M(CO)_3L_3$	C_{3v}	A_1  IR and R	E  IR and R		
<u>trans</u> - $M(CO)_3L_3$	C_{2v}	A_1  all IR and R	A_1  all IR and R	B_1  all IR and R	

NOTE:

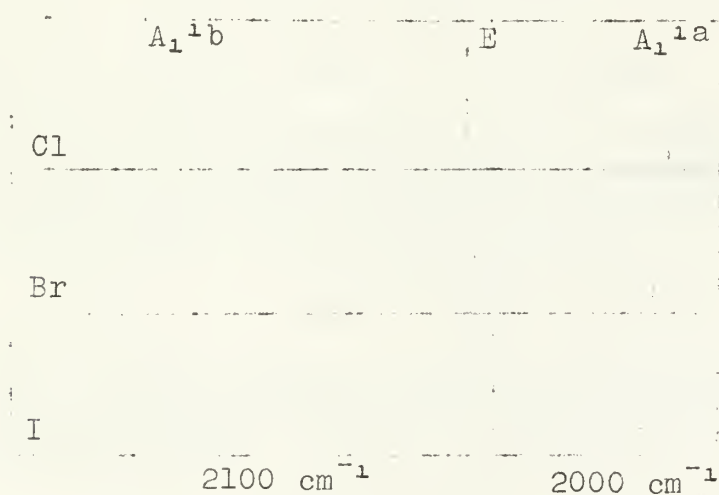
1. Arrow toward center indicates contraction of CO bond.
2. Only one component is shown for degenerate modes.
3. An A_1 mode forbidden except for interaction with another A_1 mode is listed as active.

After the spectra have been run, it is informative to match the frequencies with the theoretically predicted modes. For metal carbonyls this assignment is facilitated by the following: 1) coincidence of infrared and Raman frequencies, 2) intensity of overtones and combination bands, 3) relative energies of modes (from theoretical predictions) 4) polarization of Raman lines 5) relative intensities predicted by the nature of the mode.

The complete assignment of frequencies in the simplest compounds of this type, the chromium group hexacarbonyls, is still a matter of disagreement. The original assignments of Hawkins et. al. (31) have been redone several times (32-35) as methods improved.

Pentacarbonyl halides of Mn, Tc and Re present interesting examples of the method and problems encountered. Various workers have reported spectra of these compounds showing two, three or four CO stretching bands. Some of the apparent anomalies can be attributed to experimental methods; however, theoretical considerations have been put forth to explain others. Kaesz et. al. (8, 36) have recently studied the entire series of compounds. An example of their results is given below.

Carbonyl Stretch Frequencies and Relative Intensities in $\text{Mn}(\text{CO})_5\text{X}$



With reference to the drawing of the appropriate modes in Table IV, the following deductions are made (30,36).

1. The E mode will have an intensity roughly four times greater than A_1^{1a} . This crude approximation comes from the fact that four groups, as opposed to one, are oscillating.
2. The A_1^{1b} mode is infrared forbidden except for coupling with A_1^{1a} or for non-coplanarity of the four equivalent carbonyls. Because of the latter effect, it is predicted that the A_1^{1b} intensity

- will increase if a large halogen forces the CO groups out of the plane.
3. The A_1^{1b} frequency will be higher than that of E. More energy is required to stretch two carbonyl groups simultaneously.
 4. Due to bonding considerations, the unique, axial carbonyl is more strongly bonded to the metal. The A_1^{1a} mode is expected to be lowest in energy.

The assignments shown are consistent with all of these considerations. The small, unlabeled band is the ^{13}C mode of E.

FORCE CONSTANTS

A complete study of molecular vibrations includes an estimation of force and interaction constants (28,29). Consider first a diatomic molecule. It has a single mode of vibration. Assuming bonding forces are harmonic, the potential energy is:

$$V = 1/2 k q^2 \quad [1]$$

where k is the force constant and q is the instantaneous displacement from the equilibrium bond distance. The classical vibration frequency, ν , is then:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad [2]$$

where μ is the reduced mass of the molecule.

In more complex molecules internal coordinates, q_i, q_j, \dots , such as bond distances, bond angles and distances between non-bonded atoms define the system. The analogous equation for potential energy is:

$$V = 1/2 \sum_{i,j} k_{ij} q_i q_j \quad [3]$$

The k_{ij} are called general quadratic force constants. By the methods of normal coordinate analysis, this potential can be rewritten as:

$$V = 1/2 \sum_i \lambda_i Q_i^2 \quad [4]$$

where the constants, λ_i , are determined by secular equations in k_{ij} , and the Q_i are normal coordinates. The frequency is then:

$$\nu_i = \frac{1}{2\pi} \sqrt{\lambda_i} \quad [5]$$

The common difficulty at this point is that in all but the simplest molecules, the number of constants, k_{ij} , to be determined exceeds the number of modes. Various approximations are made in which some interaction constants are ignored or relationships between certain of them are established.

An Approximate Method. Cotton and Kraihanzel (37-39) have employed a simple vibrational model which enables them to calculate stretching force constants, k , and stretch-stretch interaction constants, k_i , for the metal hexacarbonyls and their derivatives. The following approximations have been made:

1. The carbonyl stretching modes can be separated from the other modes i.e. no coupling occurs with other modes.
2. Coupling does occur between CO groups. The mechanism is entirely non-mechanical.
3. No corrections for anharmonicity are made.

Simple valence considerations, first pointed out by L.H. Jones (42), permit useful predictions concerning the force and interaction constants:

1. CO-CO stretch interaction constants, k_i , are always positive.
2. These k_i differ depending on whether the CO groups are cis or trans to each other. The following relation is assumed:

$$k_i = k_{cis} = 1/2k_{trans}$$

3. The stretching constant, k , decreases and the interaction constant, k_i , increases as carbonyl groups are replaced by ligands making less demand for $d\pi$ electrons. The effect on k is greater in trans substitution.

Potential energy matrices are set up using standard procedures (29). The relationships between the k_i given above are applied. In all cases the secular equations which result contain a sufficiently small number of unknowns so that a solution is possible.

Cis $\text{Mo}(\text{PF}_3)_3 (\text{CO})_3$ will be discussed here as a representative of this method (39). As Table IV shows, the molecule is of C_{3v} symmetry, with two infrared active modes. The approximate secular equations are:

$$\lambda_{A_1} = \frac{1}{\sqrt{3}} (k + 2k_i)$$

$$\lambda_E = \frac{1}{\sqrt{2}} (k - k_i)$$

By application of equation [5]

$$\omega_{A_1} = \frac{1}{2\pi} \sqrt{\frac{k+2k_i}{I}}$$

$$\omega_E = \frac{1}{2\pi} \sqrt{\frac{k-k_i}{I}}$$

These two frequencies have been experimentally determined and are reported as 2090 and 2055 cm^{-1} respectively. The resulting force constants are:

$$k = 16.98 \text{ md/\AA}$$

$$k_i = 0.33 \text{ md/\AA}$$

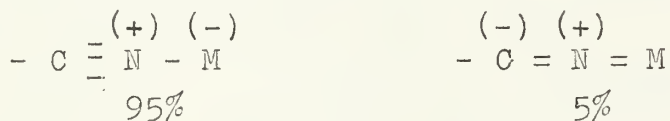
It is of interest to compare the analogous values for Mo(CO)_6 . Cotton and Kraihanzel report (37).

$$k = 16.52 \text{ md/\AA}$$

$$k_i = 0.27 \text{ md/\AA}$$

They conclude that PF_3 is a better π -acceptor than CO. This order is the reverse of that of Horrocks and Taylor discussed earlier on the basis of frequencies only.

Cotton has used the values of k and k_i to make a rough calculation of the contribution of the two canonical forms to the total bonding in a nitrile complex (39):



More precise calculations of interaction constants have been carried out, but only for the M(CO)_6 case. Because of the nature of the problem, some method of approximation is always used. Methods which have been employed by various workers are: the general quadratic valence force field ignoring lesser effects (40); the Urey-Bradley force field (41,32); the π -interaction force field (42); and the resonance interaction valence force field (43).

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"CONFORMATIONAL EFFECTS IN CHELATE RINGS"

Samuel W. Sopp

March 10, 1964

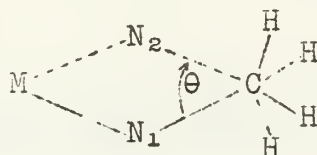
INTRODUCTION

Since the proposal by Theilacker (1) that the ethylenediamine ligand in metal-ethylenediamine chelate rings was not a planar but a puckered ring, many investigations have been conducted on the effects of this conformation. This seminar will deal with some of the recent developments in the areas of absolute structure, stability of optical isomers, and stereospecificity of some optically active ligands.

-THEORETICAL MODELS-

In order to understand the effects of ring conformation, the spatial arrangements that the individual chelate rings can assume in the metal complex must be visualized. Since the position of the donor atoms to the central metal ion only varies slightly from a regular octahedron, a consideration of only the ring atoms is necessary. The arrangement of the ring atoms in non-planar, flexible rings is important to the stereochemical properties of the metal chelate.

The geometry of the five-membered chelate rings of the diamines was accurately calculated by a method (2) using Vector analysis. The arrangement of ring atoms was chosen with the expected values for the bond distances and using tetrahedral angles about the individual atoms. The metal-chelate ring is markedly puckered. Figure 1 illustrates a view of the metal-ethylenediamine (en) ring down the C-C bond axis.



θ is the dihedral angle between the $N_1-C_1-C_2$ and $N_2-C_2-C_1$ planes in the ring. The calculated angle θ is 48° . In general, the agreement with accepted values from X-ray studies of $[Co(en)_3]^{3+}$ salts is very good (4,5). A fact to be considered is the position of groups attached to the ring atoms. These are approximately axial* and equatorial*. (*-according to Corey and Bailer's notation). The positions of the substituents are similar to those found in cyclohexane.

Other non-planar ring systems are also of importance, but since few or no analyses of their conformation have been attempted, we will limit our consideration to the five-membered chelate rings.

The notation devised by Corey and Bailar (3) in a classic paper on stereospecificity will be used for designating the conformation of the individual chelate rings. In an isolated metal-en chelate ring the puckered ring may exist in two "gauche" forms, designated as k and k', which are enantiomers. The free energy of the two forms would be equivalent, and they would have the same stability.

In a complex containing more than one chelate ring, the ligands may be arranged about the metal ion in a number of ways, since the individual ring may have either the k or k' conformation. In a system having two ethylenediamine rings in a square-planar arrangement about the metal-ion, the possibility of having kk, kk', and k'k' exists. Calculation by Corey and Bailar (3) using non-bonded interactions (basically the hydrogens on the en ring) indicate the kk form to be the most stable. Other conformations for the square-planar arrangement are possible (1,6).

The tris-complexes can theoretically exist in four possible forms; kkk, kkk', kk'k' and k'k'k'. The relative stabilities of the two extreme forms have been approximated, and the kkk is considered to be the most stable. (3) The two forms were descriptively designated as "lel" (kkk) where the carbon-carbon bonds in all three rings are approximately parallel to the short trigonal axis, and "ob" (k'k'k') where the carbon-carbon bonds are oblique to the trigonal axis.

Many interesting possibilities arise when the chelate ring itself has an asymmetric center, which in itself has optical activity. Examples of metal chelates with optically active ligands have been studied extensively; some of the most recent investigations will be discussed.

STRUCTURAL DETERMINATIONS

X-ray investigations of the crystal structure of some of the metal-chelate compounds have been conducted to determine the molecular parameters. These investigations are summarized in Table I.

TABLE I

CRYSTAL DETERMINED	ION	RING RELATIONSHIP	REMARKS	REF.
<u>trans</u> -[Co en ₂ Cl ₂]Cl·HCl·2H ₂ O	<u>trans</u> [Co(en) ₂ Cl ₂] ⁺	kk'	ion is centric	(7)
<u>trans</u> -[Co en ₂ Br ₂]Br·HBr·2H ₂ O	<u>trans</u> [Co(en) ₂ Br ₂] ⁺	kk'	same	(8)
<u>trans</u> -[Co en ₂ Cl ₂]Cl	<u>trans</u> [Co(en) ₂ Cl ₂] ⁺	kk'	same	(9)
<u>cis</u> -[Co en ₂ Cl ₂]Cl·H ₂ O	<u>cis</u> [Co(en) ₂ Cl ₂] ⁺	kk'	_____	(10)
D,L-[Co en ₂]Cl ₂ ·3H ₂ O	[Co(en) ₂] ³⁺	Dkkk and Lk'k'k' or Dk'k'k' and Lkkk	θ = 48.6°; 3-fold rotation axis;	(4)
2-D[Co en ₂]Cl ₂ ·NaCl·6H ₂ O	(+)-[Co(en) ₂] ³⁺	kkk	ion parameters similar to above; absolute configuration D; "lel"	(5,5a)
<u>trans</u> -[Co 1-pn ₂ Cl ₂]Cl·HCl	[Co(1-pn) ₂ Cl ₂] ⁺	kk	θ = 55°; -CH ₃ is equatorial; ~ 2-fold rotation axis about Cl-Co-Cl bond	(11)
(-)-[Co 1-pn ₂]Br ₃	(-)-[Co(1-pn) ₂] ³⁺	kkk	-CH ₃ is equatorial; 3-fold symmetry axis; "lel" form; same absolute configuration as L-[Co(en) ₂] ³⁺ .	(12)

Table

(1)	Description of work	Quantity	Unit	Total cost
(2)	Excavation of trench	100	m ³	1000
(3)	Laying of bricks	1000	nos	10000
(4)	Plastering of wall	100	m ²	1000
(5)	Painting of wall	100	m ²	1000
(6)	Laying of floor	100	m ²	1000
(7)	Laying of roof	100	m ²	1000
(8)	Laying of wall	100	m ²	1000
(9)	Laying of floor	100	m ²	1000
(10)	Laying of wall	100	m ²	1000

In all cases, the diamine rings were found to exist in the "gauche" conformation. The relationship of the ethylenediamine ligands to each other when in a square-planar arrangement about the metal atom was the kk' form in all cases. This is contradictory to Bailar and Corey's prediction. However, in the propylenediamine complex, the kk form was found. There is greater puckering of the propylenediamine ring ($\theta=55^\circ$) than the ethylenediamine ring (48.6°). This is presumably due to the methyl group. The methyl group was found to be in the energetically favored equatorial position. The tris-complexes are of the "1el" form as predicted (3).

The absolute configuration of two of the ions, $D(+)-[Co(en)_3]^{3+}$ and $L-(-)-[Co(1-pn)_3]^{3+}$ is confirmed by X-ray absorption edge techniques (13).

APPLICATION OF CONFORMATIONAL ANALYSIS TO STEREOSPECIFICITY

Discussions of the principles of stereospecificity can be found in recent reviews (14-17). Stereospecific limitation due to the presence of one or more optically active ligands has, in general, excluded many theoretically possible optical isomers. In the case of three asymmetric ligands, generally only the two forms L-ddd and D-lll were isolated when the racemic base was used.

Dwyer and co-workers (18) oxidized a mixture of Co(II) and 1-propylenediamine (1-pn) in acid solution and obtained two isomeric compounds. The corresponding isomers from d-propylenediamine (d-pn) were also reported. Table 2 summarizes the optical properties of the substances isolated.

Table - 2

<u>Compound</u>	<u>$[\alpha]_D$</u>	<u>$[\alpha]_{5461}$</u>
D-[Co(d-pn) ₃]I ₃ ·H ₂ O	+24°	+184°
L-[Co(d-pn) ₃]I ₃ ·H ₂ O	-214°	-404°
L-[Co(1-pn) ₃]I ₃ ·H ₂ O	-24°	-184°
D-[Co(1-pn) ₃]I ₃ ·H ₂ O	+214°	+404°

For the "reaction", "1el" \rightleftharpoons "ob", the authors calculated the $K = 1el/ob = 5.75$ and $\Delta F^\circ = -1.02 \pm .05$ Kcal/mole. This corresponds favorably with the prediction by Corey and Bailar that the "1el" isomer was the more stable.

Dwyer (19) has further studied some of the optical isomers of tris-propylenediamine. platinum (IV) ion. The reaction between $H_2[PtCl_6]$ and an alcoholic solution of d-propylenediamine gave two optical isomers of $[Pt(d-pn)_3]Cl_4$ and substantial amounts of $[Pt(d-pn)_2]Cl_2$. The compounds were separated by precipitation with oxalate ion. The two isomeric tris-complexes gave $[\alpha]_D$ -168° and +13° in 0.015N NaOH. These have been designated as L-ddd and D-ddd respectively. The relative amounts of the stable L-ddd and unstable D-ddd were of the same order as for the Co(III) complexes, 85% and 15%.

The inability of workers (20,21,22) to isolate mixed tris-diamine complexes containing d-and and l-bidentate ligands was thought of as being due to an inherent instability in those complexes. Dwyer has taken the view that an equilibrium is established among all the species during the preparative procedure.

One of Dwyer's early attempts to prepare and resolve the l-propylenediamine bis-ethylenediamine cobalt (III) salts met with failure. (23) cis or trans $[\text{Co}(\text{en})_2\text{Cl}_2]$ reacted with l-pn in H_2O , DMF, and EtOH to give only tris-en-and tris-l-pn-Co (III) chlorides. The expected mixed tris-(diamine) complexes were not isolated. The specific rotations, measured at three different wavelengths, were accounted for by equimolar mixtures of $\text{L}[\text{Co}(\text{l-pn})_3]^{3+}$ and $\text{L}[\text{Co}(\text{en})_3]^{3+}$ for the levorotatory material and $\text{D}[\text{Co}(\text{l-pn})_3]^{3+}$ and $\text{D}[\text{Co}(\text{en})_3]^{3+}$ for the dextrorotatory substance.

Recently, Dwyer, MacDermott, and Sargeson (24) have isolated the optical isomers of $\text{L}[\text{Co}(\text{l-pn})_2\text{en}]\text{Cl}_3$, $\text{L}[\text{Co}(\text{l-pn})(\text{en})_2]\text{Cl}_3$, $\text{D}[\text{Co}(\text{l-pn})_2\text{en}](\text{ClO}_4)_3$, $\text{D}[\text{Co}(\text{l-pn})(\text{en})_2](\text{ClO}_4)_3$, and the tris-isomers, $\text{L}[\text{Co}(\text{l-pn})_3]\text{Cl}_3$ and $\text{D}[\text{Co}(\text{l-pn})_3]\text{Cl}_3$ by chromatographic separation. The concentration quotients between the D- and L-isomers were $K = \text{Dl}/\text{Ll} = 0.47$, $K = \text{Dll}/\text{Lll} = 0.133$ and $K = \text{Dlll}/\text{Llll} = .0635$. The conformations that the en and pn rings adopt are used as a basis for rationalization of stabilities.

Some of the optical isomers of the "mixed" tris-(diamine) complexes of cobalt (III) iodides (25) and platinum (IV) chlorides (26) have also been isolated and their optical isomers characterized. $[\text{Pt}(\text{en})_2\text{l-pn}]\text{Cl}_4$, $[\text{Pt}(\text{en})(\text{l-pn})_2]\text{Cl}_4$, and $[\text{Pt}(\text{d-pn})_2\text{l-pn}]\text{Cl}_4$ were prepared by the reaction of tetrachloroethylenediamine- or tetrachloropropylenediamine-platinum (IV) chloride and the appropriate diamine in DMF. The optical isomers of each compound (Table 3), separated through the d- and l- tartrates, were found to show no disproportionation or racemization even in boiling aqueous solution.

Table - 3

<u>Isomer</u>	<u>$[\alpha]_D$</u>	<u>% in isomeric mixture</u>
$\text{D}[\text{Pt}(\text{en})_2\text{l-pn}]\text{Cl}_4$	+133	50
$\text{L}[\text{Pt}(\text{en})_2\text{l-pn}]\text{Cl}_4$	-74	50
$\text{D}[\text{Pt}(\text{en})(\text{l-pn})_2]\text{Cl}_4$	+176	55
$\text{L}[\text{Pt}(\text{en})(\text{l-pn})_2]\text{Cl}_4$	-29	45
$\text{D}[\text{Pt}(\text{d-pn})_2\text{l-pn}]\text{Cl}_4$	+83	65
$\text{L}[\text{Pt}(\text{d-pn})_2\text{l-pn}]\text{Cl}_4$	-158	35

The "mixed" tris-cobalt (III) isomers isolated and characterized were $\text{D}[\text{Co}(\text{d-pn})_2\text{l-pn}]\text{I}_3$, and $\text{L}[\text{Co}(\text{l-pn})_2\text{d-pn}]\text{I}_3$. In addition, the concentration constants $K = \text{Dddd}/\text{Llll}$, $\text{Llld}/\text{Dddd} = 1.0$, $K = \text{Dddl}/\text{Lddl} = 2.4$, and $K = \text{Ddll}/\text{Llld}/\text{Dlll}$, $\text{Lddd} = 6.1$ were determined. An attempt is made to correlate the stabilities of the optical isomers by conformational analysis of the possible positions of the propylenediamine rings.

In order to obtain some quantitative information as to the free energy difference between the optical isomers of complexes containing one asymmetric ligand, the anion $[\text{Co } l\text{-pn } (\text{C}_2\text{O}_4)_2]^-$ has been prepared. (27) The anion can exist only in the D1 and L1 forms. The D1 isomer predominates, $K = \text{D1/L1} = 1.63$, $\Delta F = -270$ cal/mole. The oxalato-bis-1-propylenediamine cobalt (III) iodide was also prepared, and the concentration quotient was determined, $K = \text{D11/L11} = 1.40$ and $F = -200$ cal/mole. Optical rotatory dispersion measurements show that the D1 and D11 isomers had curves similar to those of $\text{D-}[\text{Co en}(\text{C}_2\text{O}_4)_2]^-$ and $\text{D-}[\text{Co en}_2(\text{C}_2\text{O}_4)]^-$. (28)

Absolute stereospecificity has been found in metal complexes of the polyaminocarboxylic acids. The $[\text{Co}(\text{PDTA})]^-$ ion was prepared (29), and the concentration ratio determined, $K = \text{D1/Dd} > 99$ and $\Delta F^\circ > 3\text{Kcal/mole}$. No racemization was noted even when the solutions of $[\text{Co}(\text{PDTA})]^-$ were kept at 98° . Stereomodels of the sexadentate complex indicate that one isomer is sterically hindered. This was demonstrated by attaching the methyl group to various positions of the methylenic carbons. This investigation showed that the methyl group appeared in the axial position of the L-1 form and crowded the carbonyl group of the acetic acid portion attached to the nitrogen remote from the asymmetric carbon.

Busch and co-workers (30) have studied the reaction of $(-)[\text{Co}(\text{d-PDTA})]^-$ with 50% aqueous ethylenediamine and obtained the product, $\text{L-}(-)[\text{Co en}_3]$. The stereospecificity of the reaction appears to be extreme. The absorption spectrum and optical rotatory dispersion curves correspond to that of $\text{K}[\text{Co}(\text{en})_3]\text{EDTA}$. In the reaction of $(-)\text{K}[\text{Co}(\text{EDTA})]$ with 50% aqueous ethylenediamine, only 56.6% of $\text{L-}(-)[\text{Co}(\text{en})_3]^{3+}$ is found, the remainder being the $\text{D-(+)}\text{ isomer}$. Reactions of the pentadentate complexes produce similar results. The complexes $(-)-[\text{Co}(\text{EDTA})]^-$ and $(-)-[\text{Co}(\text{PDTA})]^-$ possess nearly identical rotatory dispersion curves and absorption spectra. Therefore, Co (III) complexes of EDTA and PDTA with same rotation are inferred to have the same configuration. The authors deduce that the methyl group is equatorially oriented, and the extreme stereospecificity is due to the difference in energy of the axial and equatorial positions on the asymmetric carbon.

Busch and Cooke (31) further infer the absolute configuration of a series of EDTA and PDTA complexes by chemical transformations within the group and those arising from conversion to $[\text{Co}(\text{en})_3]^{3+}$. The configurations are considered along with free propylenediamine to infer the conformation of the chelate ring in the metal complex.

CONCLUSION

This seminar has attempted to show that conformational analysis of non-planar chelate rings can be an important tool for predicting reaction products, stability of optical isomers, and reaction mechanisms.

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RECENT ADVANCES IN THE COMPLEX CHEMISTRY OF RHODIUM (III)

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March 17, 1964

I. Introduction

From both the theoretical and experimental aspects, the coordination chemistry of the first transition series is much better known today than is that of the second and third series. This is particularly true of the d^6 case where cobalt (III) is known through a wide variety of complex compounds, whereas relatively little is known of the chemistry of rhodium (III) and iridium (III).

There has been, however, an increasing amount of work done on the complex chemistry of rhodium (III) in the past few years. Perhaps the most interesting of this work has attempted to draw comparisons with cobalt (III) and then explain these comparisons on theoretical grounds. While we would expect similarities to exist between cobalt (III) and rhodium (III) because of electronic arrangements, we would expect differences to result from at least three factors: 1) the larger size and hence smaller charge to radius ratio of rhodium (III), 2) the larger crystal field splittings of rhodium (III), and 3) the lack of a readily accessible lower oxidation state for rhodium (III).

II. Preparation

The most common starting materials for preparation of rhodium (III) complexes are $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and freshly prepared rhodium hydroxide. Johnson and Basolo (1,2) have recently used $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ as a starting material in preparing several diacidotetraammines (compounds of the type $[\text{RhA}_4\text{X}_2]^+$, where A_4 signifies coordination of four of the six octahedral positions by amine nitrogens and $\text{X}^- = \text{I}^-, \text{Br}^-, \text{SCN}^-, \text{NO}_2^-, \text{N}_3^-, \text{OH}^-$, etc.). It is interesting that only two attempts to prepare geometrical or optical isomers of the dichlorotetraamminerhodium (III) type have been successful, even though such isomers are found quite commonly in the case of cobalt (III) (1,2).

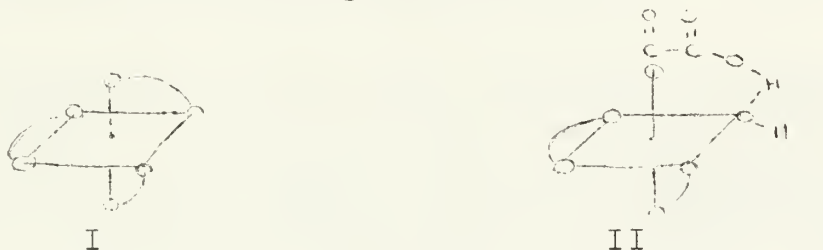
Rhodium hydroxide has been used to prepare, for example, $[\text{Rh}(\text{H}_2\text{O})(\text{HEDTA})]$ (3), and $[\text{Rh}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ (4). This latter complex is interesting in that it represents the only well defined and characterized aquo species in the second or third transition series.

III. Structure

With two possible exceptions, the complexes of rhodium (III) are all octahedral. They are, furthermore, diamagnetic as would be expected from the larger crystal field splitting of rhodium (III) as compared to cobalt (III). The spectra of the complexes of cobalt (III) and rhodium (III) are therefore similar, possessing bands due to $^1\text{A}_{1g} - ^1\text{T}_{1g}$ and $^1\text{A}_{1g} - ^1\text{T}_{2g}$ transitions (5).

These bands, together with accompanying charge transfer bands, give rise to the orange to brown colors generally characteristic of rhodium (III) complexes. The analogous spectral behavior of cobalt (III) and rhodium (III) complexes is often useful in structural assignment of rhodium (III) compounds. It has been noted, for example, that in the diacidotetraamminerhodium (III) complexes, the cis isomers exhibit the more intense UV bands just as with the analogous cobalt (III) complexes (2). The IR spectra are also similar, the cis isomers of rhodium exhibiting the greater degree of splitting just as with the cobalt (III) complexes.

Porte and Gutowsky (6) have recently investigated the structure of $K_3[Rh(C_2O_4)_3] \cdot 4 \frac{1}{2} H_2O$ by use of NMR. Whereas simple hydrates show only two proton resonance peaks, this compound showed three. This led to the conclusion that this complex actually exists as an equimolar mixture of structures I and II. This structure is also consistent with oxalate exchange studies (7).



The reported examples of five coordinate rhodium (III) are $[Rh(1\text{-naphthyl})_2 L_2 Br]$ where L is tri-(n-propyl) phosphine or diethylphenylphosphine (8). These compounds are monomeric, diamagnetic, and have dipole moments of approximately 3D. Since rhodium (III) is normally six-coordinate, these compounds might be expected to be liable to attack by nucleophilic reagents. Their stability has been attributed to a very compact arrangement of ligands around the metal atom which then completely shields it from attacking reagents.

IV. Reactions

It has been generally noted that rhodium (III) complexes have a greater resistance to ligand replacement, isomerization and racemization than do their cobalt (III) analogs (2,9,10, 11). A recent study (11) on the rates of hydrolysis of certain chloroamine-rhodium (III) complexes allows several other interesting comparisons between cobalt (III) and rhodium (III) to be made. It is found that just as in the case of cobalt (III), the rate of acid hydrolysis increases with an increase in alkyl substitution on ethylenediamine. Increasing the number of chelate rings likewise has the same effect on rhodium (III) as it does on cobalt (III). It is also found that the rate of reaction of $trans-[Rh en_2 Cl_2]^+$ with a variety of nucleophilic reagents is independent of the nature of the incoming ligand. Three striking differences between the rhodium (III) and cobalt (III) systems are found, however: 1) the rate of reaction of a rhodium (III) complex is insensitive to the charge on the complex,

2) alkali has little or no effect on the rate of hydrolysis, and 3) reactions of rhodium (III) complexes occur with almost complete retention of configuration. These last three observations have led to the suggestions that rhodium (III) complexes react by a cis bimolecular displacement reaction and that π -bonding is less important in rhodium (III) than it is in cobalt (III).

While chloroammine-rhodium (III) complexes generally react only quite slowly by nucleophilic displacement, several of these complexes have been found to react quite rapidly with sodium borohydride to give hydride species (12, 13). These complexes were studied by NMR, UV and, when the tetraphenylborate salts could be isolated, also by IR. Such species might be responsible for the hydrazine catalyzed reactions of $[\text{Rh en}_2\text{Cl}]^+$ with chloride ion and of $[\text{Rh en}_2\text{Br}]^+$ with bromide ion. Rhodium (II) catalysis or reduction to rhodium (I) and reaction via a Rh(I) - Rh(III) bridged intermediate are also possible, however. (14).

Other rate studies on the amine complexes of rhodium (III) include an investigation of the rates of hydrogen exchange of $[\text{M}(\text{NH}_3)_6]^{3+}$ where $\text{M} = \text{Co}, \text{Rh}, \text{and Ir}$ (15) and the acid catalysis of acetatopentammine complexes of these same three metals (16). Barton and Harris (7) have studied the oxalate exchange and aquation reactions of the trisoxalatorhodate (III) ion. There has also been some evidence for the photoracemization of this ion at 24° with light of 546 m μ (17).

Photoracemization has also been noted to occur fairly readily in the case of $[\text{Rh}(\text{EDTA})(\text{H}_2\text{O})]^-$ (3). It has furthermore been observed that there is a photoinduced mutarotation of $\text{L-}[\text{Rh}(\text{H}_2\text{O})(\lambda\text{-H-PDTA})]\cdot\text{H}_2\text{O}$ (18). This latter reaction appears to be reversible since the solution regains its optical activity completely after standing in the dark for two days.

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Recent Chemistry of the Nitrogen and Sulfur Fluorides

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April 7, 1964

Chemistry of the -NF_2 Group

I. Introduction

The report by Colburn and Kennedy (1) in 1958 of the synthesis of tetrafluorohydrazine initiated an extensive investigation of all phases of nitrogen-fluorine chemistry which has continued until present.

There have been a number of thorough reviews published on the nitrogen fluorides, the three latest of which are by Hoffman and Neville (2), Colburn (3), and Pankratov (4). These reviews represent a variety of approaches and emphases, although all of them present a good summary of the fundamental structures and properties of the nitrogen fluorides.

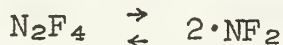
One of the most interesting aspects of the present work in this field centers around reactions of nitrogen fluorides containing the -NF_2 moiety. The preparations and structures of the two most reactive compounds in this category, N_2F_4 and HNF_2 , will be mentioned, and the nature of the $\cdot\text{NF}_2$ radical will be discussed. Finally, some typical reactions of these compounds will be presented, showing both their ability to act as a source of $\cdot\text{NF}_2$ radicals and as oxidants.

II. Synthesis and Structure of N_2F_4 and HNF_2

A. N_2F_4

Tetrafluorohydrazine has been synthesized in quantity by five known methods summarized by Pankratov (4). All involve the reaction of NF_3 over metal catalysts. The hydrazine-like structure of N_2F_4 was established by mass spectra and n.m.r. (5), as well as by a microwave study by Lide (6). A recent detailed vibrational analysis of the infrared spectrum (7) has supported Lide's work.

The N_2F_4 molecule serves as a major source of $\cdot\text{NF}_2$ radicals by dissociating in the following manner:



This equilibrium reaction was first studied by Colburn (8). Since then, dissociation data for the above equilibrium has been obtained by four different methods: ultraviolet spectroscopy, pressure vs. temperature studies, e.p.r., and mass spectra, all of which have been summarized by Colburn (3). These methods give an overall best value of $\Delta H_{\text{diss.}}$ for N_2F_4 of 20.0 ± 1 kcal/mole (9).

B. HNF_2

Difluoroamine was first prepared and positively identified by Kennedy and Colburn (10) but can be more easily prepared by the reaction of thiophenol with N_2F_4 (11), by direct fluorination of urea (12), or by the reaction of trityldifluoroamine, $\phi_3\text{-C-NF}_2$, and H_2SO_4 (13).

Detailed structure work on this molecule has been done by Lide (14), (15).

III. The $\cdot\text{NF}_2$ Radical

The original structure work on the difluoroamine radical was done by Lide *et al.* (16) using infrared spectroscopy combined with known NF_3 and hydrazine bond distances. Their conclusions have been re-interpreted in terms of HNF_2 dimensions (14).

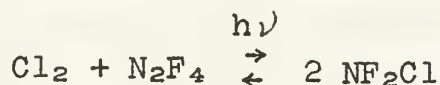
Since the source of $\cdot\text{NF}_2$ radicals, N_2F_4 , is only 0.05% dissociated at room temperature and pressure (9), the best e.p.r. work has been done on $\cdot\text{NF}_2$ trapped in liquids (17) and molecular sieves (18). This work has shown $\cdot\text{NF}_2$ to be a bent triatomic molecule containing one unpaired electron in a relatively pure p level and having small s character with respect to the central atom (17). A simplified interpretation of the single ultraviolet peak of $\cdot\text{NF}_2$ as being due to a forbidden $n_{\text{N}} \rightarrow \pi^*$ transition was made by Johnson (9). Thermodynamic functions $^{\circ}\text{N}$ for $\cdot\text{NF}_2$ are reported by Harmony and Meyers (19).

IV. Reactions

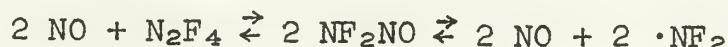
A. Radical Reactions of N_2F_4

Colburn reports numerous reactions of N_2F_4 in which this compound acts as a source of the $\cdot\text{NF}_2$ radical (3). Freeman has pointed out that the first $\cdot\text{NF}_2$ reaction was the original hot-tube preparation of N_2F_4 itself from NF_3 by radical coupling (20). One of the first reactions of N_2F_4 acting as a radical source was its reaction with thiophenol and arsine to form HNF_2 (11). These reactions require either high temperature or ultraviolet light, both of which are typical of radical reactions.

One of the earliest ultraviolet-catalyzed reactions studied was the equilibrium:



reported by Petry (21). Later Colburn and Johnson observed the reaction of NO with N_2F_4 (22) and did a detailed gas phase study (23) on the equilibria:



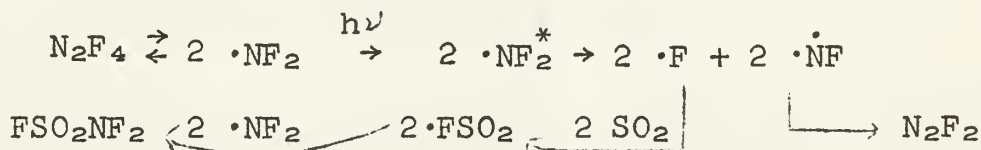
Frazer et al. have reacted N_2F_4 with CF_3I in ultraviolet light to form CF_3NF_2 by a proposed reaction involving $\cdot NF_2$ (24). They also proposed the existence of the above $NONF_2$ entity sometime before Colburn (24).

Tetrafluorohydrazine has recently been allowed to react with peroxydisulfuryldifluoride ($S_2O_8F_2$) to give F_2NOSO_2F (25) which, in view of the recently established $\cdot SO_3F$ species (26), is undoubtedly the result of a radical coupling reaction.

Recently, Logothetis et al. (27), Cady (28), and Brey and co-workers (29) have reported the synthesis of SF_5NF_2 by the coupling of the $\cdot SF_5$ radical with N_2F_4 .

B. Radical Reactions of HNF_2

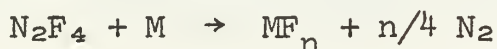
Difluoroamine, in addition to forming N_2F_4 by metal catalysis (12), has been observed by Bumgardner and co-workers to catalyze the deamination of primary amines, possibly via a $\cdot NF$ (fluorazene) intermediate (30). To strengthen this assertion, he and Lustig performed the following decomposition study of the $\cdot NF_2$ radical (31):



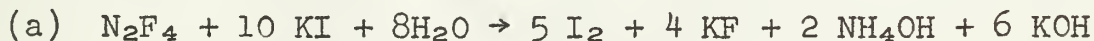
Freeman (20) has also proposed that the reaction of $ClNF_2$ with HgR_2 to give RNF_2 and N_2F_4 (3) may be a radical reaction.

C. Oxidation Reactions of N_2F_4 and HNF_2

Colburn has both stated (3) the oxidizing power of N_2F_4 and implied (11) it in describing the evolution of nitrogen as a side reaction in some of his N_2F_4 experiments. However, Pankratov was the first to propose a specific reaction to account for this non-radical behavior of N_2F_4 in terms of a simple metallic fluorination reaction. He believes the above mentioned reactions of Colburn which evolved nitrogen are of the type:



and has offered the following set of simultaneous reactions (4) as additional evidence:

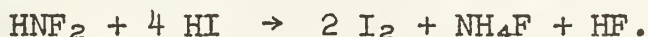


in which N_2F_4 acts as an oxidant in both cases as well as a normal fluorinating agent in (b).

Pankratov has proposed two general rules for the mode of reaction of N_2F_4 in a given situation (4) depending upon the substrate:

- (1) Reaction with a substrate containing an odd number of electrons causes radical type behavior by N_2F_4 .
- (2) Reaction with substrates having an even number of electrons gives rise to a regular fluorination accompanied by oxidation.

The reaction of difluoroamine as an oxidizing agent is amply illustrated by the following reaction (32):



V. Conclusions

Both the existence and the structural features of the $\cdot\text{NF}_2$ radical are well established. The radical-type reactions of N_2F_4 and HNF_2 are well developed and qualitatively understood, but their full utilization, especially in the field of organic chemistry, is yet to be realized. Much work remains to be done on the question of the oxidation-fluorination behavior of N_2F_4 .

Chemistry of the $-\text{SF}_5$ Group

I. Introduction

There are two reviews of sulfur-fluorine chemistry covering work done up through 1960, those of Cady (33) and Roberts (34). A general review by Feistel in 1961 (35) put a special emphasis on carbon-sulfur-fluorine chemistry, and combined with the review of SF_4 chemistry by Smith in 1962 (36), offers a thorough summary of the reactions of SF_4 and its alkyl derivatives. However, while interest in S(IV)-fluorine chemistry has diminished of late, much work has been done on S(VI)-fluorine chemistry; specifically the formation and reactions of SF_5X compounds where X represents some electronegative substituent.

In this section the modes of preparation of the $-\text{SF}_5$ group will be discussed, and then work done on the structure and nature of the bonding of the $-\text{SF}_5$ species will be reviewed. Finally, exemplary syntheses and reactions of the SF_5X compounds will be given with an emphasis on the reactions of the $\cdot\text{SF}_5$ radical.

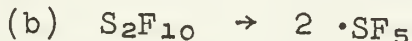
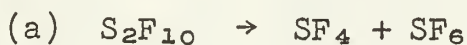
II. Modes of Preparation

The "parent" compound, SF_6 , can be synthesized by first burning sulfur in fluorine and then destroying the lower fluorides with base (37). The preparation of sulfur(VI) fluoride is now in Inorganic Syntheses (38). Other preparative methods for this compound will be discussed later.

The SF_5X compounds can be obtained by two different means. The first is an oxidative addition of some fluoride, X-F , to the SF_4 molecule at elevated temperatures which, for example, has given in the

case of Cl-F, the molecule SF_5Cl (39). A somewhat analogous reaction has been noted for SF_4 with N_2F_4 , but this time using ultraviolet light, to give SF_5NF_2 (27). It is obvious that the nature of the X-F group will limit the utility of this reaction as a general preparative method.

An alternate route to the SF_5X compounds is through the $\cdot\text{SF}_5$ moiety, which was first proposed by Trost and McIntosh (40) in the thermal decomposition of S_2F_{10} . They proposed two probable schemes for this decomposition:



of which (b) was deemed more important.

Decomposition of SF_5X (where X is an electronegative group) into two radical species can also act as a source of $\cdot\text{SF}_5$, as was illustrated for SF_5Cl by Roberts (34).

III. Structure and Bonding in $-\text{SF}_5$ Compounds

Before going into reactions, the structural features of several sulfur fluoride compounds important to this approach will be considered as well as the general S-F, S-X bonding phenomena.

A. S_2F_{10}

The structure of this compound is described in detail by Roberts (34), and consists of two SF_5 square pyramids coupled by a S-S bond of 2.21 Å length. As previously mentioned, homolytic cleavage of this bond can give two $\cdot\text{SF}_5$ radicals (40).

B. SF_6

The octahedral structure of SF_6 is also well defined by Roberts (34). It is characterized by an extreme kinetic stability, although having a ΔH_f° of 288.9 kcal/mole, and a high activation energy to reactions such as hydrolysis. However, as shall be shown, it is not totally inert to attack (41).

C. N.m.r.

N.m.r. is rapidly becoming one of the most important tools in analyzing the structure of $-\text{SF}_5$ compounds. The ^{19}F n.m.r. spectra of these compounds are generally quite complex, giving an AB_4 spectrum with the apex (A) atom split into nine separate peaks and the four base (B) atoms split into a single broad doublet (42). Cady *et al.* have found that each peak of the four base atoms is split further into six peaks giving a total of twenty-one discrete resonance frequencies for the $-\text{SF}_5$ group (43). They give complete instructions for the analysis of $-\text{SF}_5$ spectra. Explicit analyses of the ^{19}F spectra of several alkyl sulfur pentafluorides has recently been

published (44). A more thorough compilation of current ^{19}F n.m.r. work in sulfur fluoride systems is contained in a recent review by Herlocker (45).

D. Bonding

The nature of the bonding in SX_6 compounds was first treated in an elementary and generalized manner by Craig, Orgel and co-workers (46) to show the ineffectiveness of the normal overlapping power of the d orbitals and the need to contract them in order to make them compatible with bonding. They suggested that highly electronegative ligand atoms might accomplish this. This was later qualitatively shown by the use of a potential field of six negative unit charges octahedrally arranged around a d electron system (47). This arrangement gives rise to an energy-minimizing effective nuclear charge change for a single d electron from a free atom value of one unit to a bound value of three units of charge. Thus the radical maximum is reduced from nine to three atomic units, and d orbital bonding becomes feasible.

A more thorough treatment of the $3d$ radial wave function in a molecular field has also been carried out (48) treating the sulfur-fluorine $3s$, $3p$, and $3d$ orbitals explicitly by using an electrostatic field approximation. However, comparisons of the relative sulfur bonding ability of fluorine, chlorine, carbon, nitrogen and oxygen have also been made (49) which suggest that the electronegativities of these elements on the Pauling scale is not as good of a measure of their relative bonding abilities as previously thought.

IV. Reactions

A. SF_6

While often considered inert, SF_6 has been shown to be thermodynamically unstable with respect to hydrolysis (34). But, as previously mentioned, it is protected from hydrolysis by a high activation energy which is accounted for by the inability of SF_6 to undergo an $\text{S}_\text{N}2$ attack by a nucleophile. However, Case and Nyman have shown that electrophilic attack (41) by AlCl_3 and SO_3 is possible, giving respectively, AlF_3 and SO_2F_2 at temperatures of around 200° .

B. S_2F_{10}

The initial work by Trost and McIntosh on the decomposition of S_2F_{10} (40) proposed a radical dissociation into $\cdot\text{SF}_5$ groups. This radical was shown to be present mechanistically by George and Cotton (50) in their high temperature reaction of S_2F_{10} with Cl_2 to get SF_5Cl . The monochloro and monobromo compounds have also been prepared by reaction of S_2F_{10} with BCl_3 and Br_2 , but no reaction with $(\text{CN})_2$ or NO was observed (51). S_2F_{10} , when irradiated with ultraviolet light, has combined with SO_2 to form $\text{SF}_3\text{OSO}_2\text{F}$ (52). It is important to note that some of the above products are in equilibrium with the starting materials (eg. SF_5Br exists mainly as S_2F_{10} and Br_2 at room temperature) and, furthermore, that S_2F_{10} can be thought of as being a pseudohalogen lying between Br_2 and I_2 in reactivity (53). In

reactions analogous to those of SF_5Cl , Roberts has demonstrated a low efficiency, ultraviolet-catalyzed reaction between S_2F_{10} and olefins (54).

C. SF_5Cl

This compound is the most versatile of all for radical reactions and can be prepared from S_2F_{10} and Cl_2 (see above), or better by the reaction of SF_4 and ClF (55), and most recently by the reaction of SF_4 and Cl_2 in the presence of CsF (56).

Ionic Behavior. Roberts (34) has demonstrated the low stability of SF_5Cl to basic hydrolysis, and in explanation suggested an ionic mechanism involving hydroxide attack at a partially positive chlorine thus creating an SF_5^- anion. This is supported by later work which shows that SF_5Cl will chlorinate benzene under Friedel-Crafts conditions (34) and by Tullock *et al.* (56), who propose Cs^+SF_5^- as an intermediate in the synthesis of SF_5Cl from SF_4 , Cl_2 and CsF . The existence of a stable SF_5^- anion has recently been shown by Tunder (57) who synthesized $[(\text{CH}_3)_4\text{N}]^+[\text{SF}_5]^-$ from $(\text{CH}_3)_4\text{NF}$ and liquid SF_4 .

Radical Behavior. Roberts has also proposed a radical mechanism for SF_5Cl reacting with olefins by separating into $\cdot\text{SF}_5$ and $\cdot\text{Cl}$ radicals. Both of these then attack olefinic bonds (34) thus giving a self-perpetuating reaction. In addition, he has demonstrated radical coupling between SF_5Cl and O_2 (58) as follows:



Cady and Merrill (59) have further shown that the above peroxide undergoes the following dissociation: $\text{SF}_5\text{OOSF}_5 \rightleftharpoons 2 \text{SF}_5\text{O}\cdot$ and demonstrated this behavior in numerous reactions.

It has also been suggested by Roberts (54) that the "reduction" of SF_5Cl by H_2 proceeds via a scavenging of $\cdot\text{Cl}$ radicals by $\cdot\text{H}$, thus allowing S_2F_{10} to form readily.

SF_5Cl has been shown to react with N_2F_4 in a radical manner (27) to produce SF_5NF_2 , and the formation of adducts between SF_5Cl and amines at -78° has been reported (60). These adducts evolve one molar quantity of SF_4 upon warming to room temperature leaving behind an unidentified solid.

Most recently, azomethines, isocyanates, and isothiocyanates have been produced by the radical reaction of SF_5Cl with R-CN groups to form the $\text{R-N}\equiv\text{C}$ moiety (56). Also N -substituted SF_5 -amides can be made by metathesis of the mercurial derivatives of the above azomethines.

V. Conclusions

The general ability of S_2F_{10} and SF_5Cl to act as a source of the SF_5 moiety in reactions is well established; however, there is a need for further definitive work in some areas to differentiate between the ionic and radical reactions of SF_5Cl and related compounds. The

ultraviolet-catalyzed reactions of S_2F_{10} with the pseudohalogens has received very little study as has the nature of the equilibrium existing between products and reactants for several of the SF_5X species. Some quantitative work needs to be done in order to investigate Craig's predictions about the stabilities of different ligands on sulfur relative to fluorine. Finally, the reactions of functional groups attached to $-SF_5$ have received very little attention until recently and will no doubt be the subject of much of the future work in this field.

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SOME INORGANIC RING SYSTEMS: STRUCTURE AND BONDING

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April 21, 1964

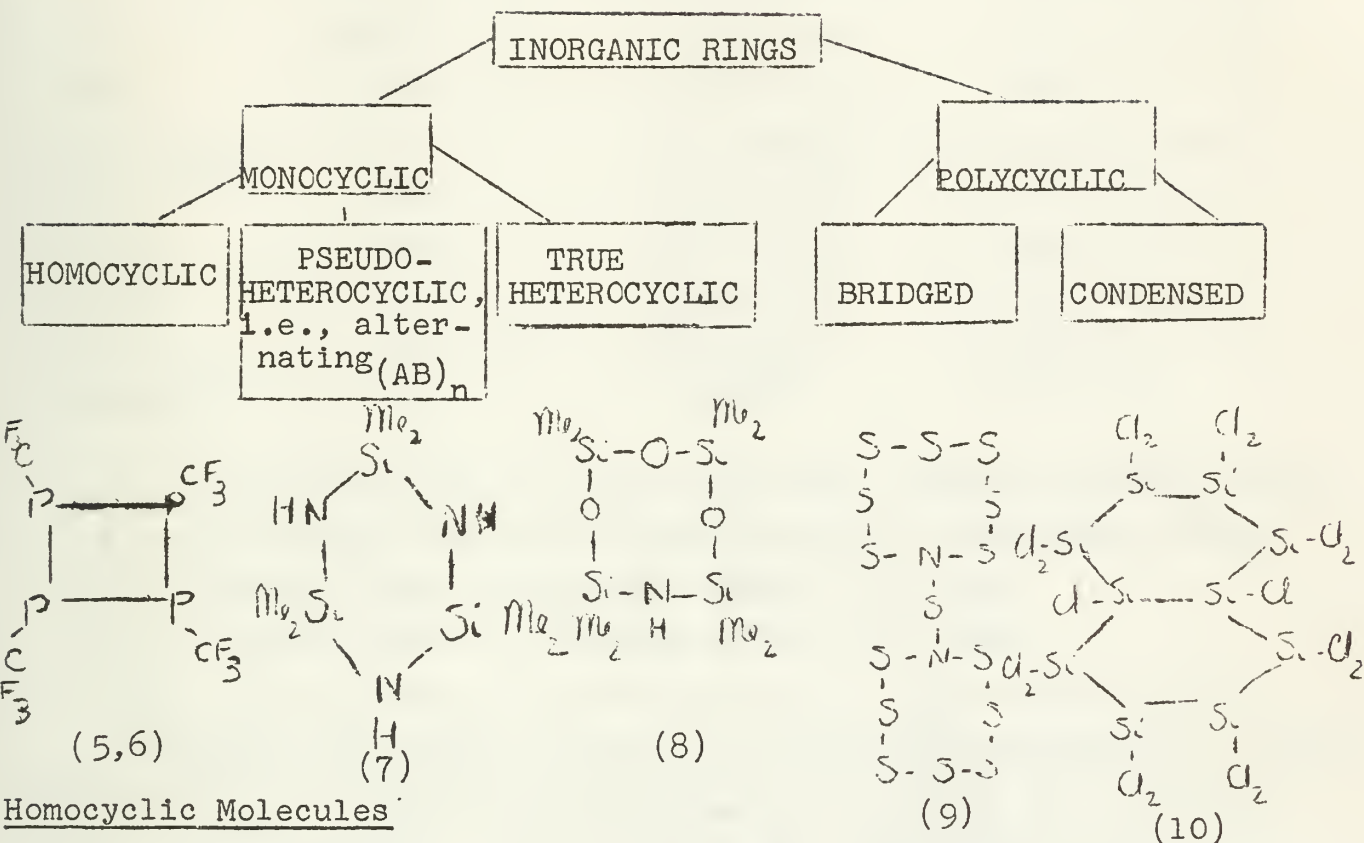
Completely inorganic polymers and macromolecular organic derivatives of inorganic main chains have aroused much interest because of their valuable technical properties and their potential as challenging species for modern bonding theories. The usual organic polymer production methods, polymerization of an unsaturated monomer or polycondensation reactions, are not useful for the formation of inorganic polymers. One well-known method of preparation uses small inorganic rings which open under appropriate conditions to produce oligomers, telomers, and polymers. The inorganic ring should not be considered merely a convenient starting material, although its tremendous value in this function cannot be denied. Due to the overwhelming number of carbon ring systems, it is easy to overlook the interesting chemistry, structure and bonding of systems not containing carbon. It is the purpose of this seminar to present a method of classification of the known inorganic rings, to consider recent structural work on the homocyclic phosphorous and arsenic rings, and to discuss the bonding schemes proposed by Craig and Dewar for cyclic $(AB)_n$ polymers, where A is a row one element and B a row two element. Time permitting, the "electron on a sphere" model for the heterocyclic S_4N_4 molecule will be outlined.

From a consideration of Pauling's electronegativity scale, and of the fact that carbon with $X_C = 2.5$ readily forms chains and rings, Haiduc (1) speculates that inorganic chains and rings of AB units can be prepared if the arithmetic mean of the individual electronegativities of A and B is \bar{X}_{A-B} is 2.5 ± 0.35 . Table I indicates \bar{X}_{A-B} for several pairs of atoms.

Table I: Mean Electronegativities

(X_{element})	B(2.0)	C(2.5)	Si(1.8)	P(2.1)	S(2.5)	Ge(1.8)	As(2.0)	Se(2.4)
O (3.5)	2.75	3.0	2.6	2.8	3.0	2.6	2.75	2.85
N (3.0)	2.5	2.75	2.4	2.6	2.75	2.4	2.5	2.7
S (2.5)	2.25	2.5	2.15	2.3	2.5	2.15	2.25	2.45
				Sb(1.9)				
				2.8				
				2.55				
				2.3				

This table provides only a qualitative scheme for predicting whether polymers containing the A-B bond may form. It must be kept in mind that homocyclic chains or rings predicted on the basis of electronegativity alone to be unstable with respect to loss or gain of electrons can be stabilized by the presence of substituents and higher order bonding.



Homocyclic rings of Si(11, 12), Ge(13), N(14), Sn(15), P(5, 6, 16-19, 26), As(19-22), S(23-25) and Se(24) are known. References are given to recent chemical, structural, and theoretical thermodynamic work for four-, five-, six-, and eight-membered rings of the above elements. Phosphorous and arsenic rings will be considered in detail.

Among the cyclic compounds of tervalent phosphorous, the most notable are the trifluoromethyl compounds $(CF_3P)_4$,⁵ prepared by the reaction of Hg with CF_3PI_2 at room temperature or by thermal decomposition of $P_2(CF_3)_4$ or $(CF_3)_2PH$. The reaction at room temperature yields 40% pentamer and 60% tetramer. No open chained polyphosphines were noticed in any of the preparations. Crystal structure determinations show a four-membered ring which is far from planar for the tetramer, and a sterically distorted pentagon for the pentamer. The molecular constants are shown in Table II.

Table II

	Tetramer	Pentamer	
		Average e.s.d.*	Range
P-P bond	2.213±0.005Å	2.223±0.017Å	2.202 to 2.252Å
P-C	1.867±0.014	1.906±0.020	1.873 to 1.925
C-F	1.335±0.015	1.346±0.032	1.281 to 1.401
P-P-P angle	84.7°	101.3±4.9° [#]	93.9° to 108.3°
P-P-C	97.8	97.6±3.9° [#]	94.2 to 107.8
P-C-F _i	118.1	116.4±1.2	114.5 to 120.0
P-C-F _o	109.6	109.2±2.4	107.0 to 111.0
F-C-F	105.7 and	107.1±2.4	103.9 to 111.9
(P-P)-(P-P)	34	37±16° [#]	18 to 58

* - standard deviation of the individual values from the average

- significant differences exist among the individual values

F_i - fluorine atoms projecting inside the rings

F_o - fluorine atoms projecting outside the rings

A bonding theory was not proposed following the crystal structure study as the P-P distances are essentially the same here and in all substances where widely different types of s-p-d or σ - π combinations can be invoked. In both rings the orientation of the CF₃ groups about a P-C bond is staggered. The actual configuration results from a balance among strains in the bond angle and the torsion angles, plus repulsions across the rings between various substituent groups.

The first arsenic ring structure was unequivocally established in 1957, when it was found that arsenomethane formed a 5-membered ring, (AsMe)₅. Although it is less distorted than (CF₃P)₅, as expected, the average angles P-P-P (101.8 ± 3.0°) and As-As-As (101.3 ± 4.2°) are the same. The non-planarity of the rings is attributed to deviation from the 108° angle of an equilateral isogonal pentagon and to the relief of Pitzer (torsion) strain. The symmetry of the stable configuration of both the As₅ and P₅ rings is between 2(C₂) and m(C_h).

Arsenobenzene is a hexamer of As atoms in a chair conformation, a phenyl group attached to each arsenic is the "radial" position. The crystal packing is efficient and steric repulsions between phenyl hydrogens allow the molecule to possess only a center of symmetry.

Pseudo-Heterocyclic Molecules

The literature on phosphonitriles, borazoles and cyclosiloxanes is copious. Thiazyl halides and cyclosilazanes are of current interest. The bonding theories proposed by Dewar, et al. (27), Craig and Paddock (28, 29), and extended by Craig (30) have been tested on the phosphonitriles because of the amount of data available, but are equally applicable to any n-membered ring of alternating A (Row 1) and B (Row 2) atoms. Both theories concern a π -bonding system brought about by d_{π} - p_{π} interaction, the differences arising from the determination of the significance of particular d orbitals.

The following diagrams will be useful references in discussion of the two theories.

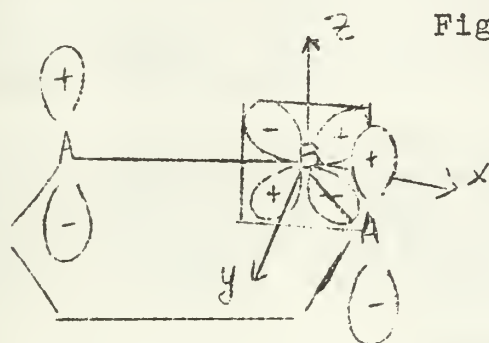


Fig. Ia. Overlap scheme for ring π -bonding (d_{xz}).

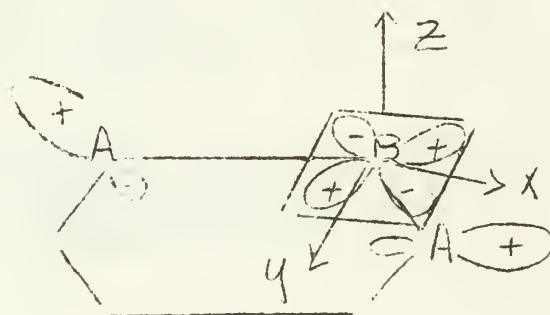


Fig. Ib. Overlap scheme for ring π' -bonding (d_{xy}).

Dewar, et al:

A linear combination of the d_{xz} and d_{yz} orbitals, both considered to contribute to d_{π} interaction, is made. A LCAO-MO treatment combines the latter with the p_z orbital of A. Each of the combination-orbitals overlaps efficiently with the 2p orbitals of just one of the neighboring A atoms, forming sets of three-centered molecular orbitals. Since the MO's overlap weakly, the π electrons are localized in islands of charge with nodes at the B atoms. As a consequence, the system is formally like an allyl cation. The resonance stability is directly proportional to the number of 3-centered bonds, i.e., to the degree of polymerization. The heat of formation of units is independent of the size of the ring. When the deviation from planarity is treated as a perturbation, the puckering of the ring is found to have little effect on the resonance energy.

Craig, et al:

On the basis of symmetry conditions and extent of overlap, the original proposal considered only d_{xz} - p_{π} interaction to be of importance and illustrative of a "new type of aromaticity" peculiar to inorganic rings of the (AB) type. A simple MO treatment led to the filling of energy levels with the lowest level doubly degenerate, exactly opposite to the order in benzene. This p_{π} - d_{π} delocalization thus leads to the loss of dominance of the sextet, and larger

rings are feasible as long as bond strain permits. In addition, $d_{\pi} - p_{\pi}$ delocalization is less sensitive to ring puckering than $p_{\pi} - p_{\pi}$ delocalization since the d orbital is larger, more polarizable and easily adapts itself to the necessary geometry.

Lone pair delocalization from A to give additional π character to the A-B bond is considered in a refinement of the theory. See Figure Ib. The new d_{π} -lone pair interactions are also dependent upon overlap, and particular ring conformations arising from steric repulsions may enhance the supplementary π interaction to the extent where, since the latter is symmetrically analogous to $p_{\pi} - p_{\pi}$ interactions, an alternation in properties with increasing ring size is observed. In spite of the fact then that unequal use of d_{xz} and d_{yz} orbitals in π bond formation always leads to completely cyclic delocalization, the change of apparent π electron stabilities with increasing ring size must also be dependent upon the effects of lone pair delocalization, improved overlap with increasing ring size, and decreasing strain energy.

A few general conclusions can be drawn about the cyclosiloxane systems in light of these two theories. Although unsaturation is not formally required in the ring, the extent of π bonding can be assessed by comparison with the tetraalkylorthosilicates in which the Si-O bond is probably nearly singular.

Table III

	Si-O	Si-C	Si-O-Si	O-Si-O	C-Si-C	Ref.
$(Me_2SiO)_3$ (el.-diff.)	1.66 ± 0.04 Å	1.86 ± 0.04 Å	$125 \pm 5^\circ$	$115 \pm 5^\circ$	$112 \pm 6^\circ$	32
(x-ray)	1.61	1.99	136	104	106	31
$(Me_2SiO)_4$	1.65	1.92	142.5	109	106	33
Pauling	1.83	1.94				34
Schomaker, Stevenson	1.76	1.88				34
Si(OMe) ₄	1.64 ± 0.03		Si-O-C 113 ± 2	113		34

Bond length is obviously not an informative factor with regard to degree of π -bonding. That the base strengths of the siloxanes (35) are much less, and the angles at O much greater than in $Si(OR)_4$, accompanied by an increase in average bond energy, however, provides positive evidence. π bonding of necessity increases ring strain. It is therefore localized, and found only to the extent that the lone pairs on the electronegative O can delocalize in the π and π' systems. Configuration is controlled by the nonbonded interactions. Hexamethylcyclotrisiloxane is found to be a planar six-membered ring, (31); octamethylcyclotetrasiloxane is a puckered eight-membered ring (33).

Similar conclusions can be drawn for the cyclosilazanes. Planar $(H_3Si)_3N$ is a well known example of π bonding in Si-N systems. IR and Raman data show that the N lone pair electrons are somewhat delocalized through the Si 3d orbitals in $(Me_2SiNH)_3$ and $(Me_2SiNH)_4$ such that the bond order of Si-NH-Si is 1.18 (36). The spectral data lead to a planar six-membered ring for $(Me_2SiNH)_3$, but electron diffraction patterns show both the trimer and tetramer as puckered rings (37). All $(AB)_4$ systems show minimum symmetry of a tetrahedron. Craig points out that interaction can easily lead to any of the crown, saddle, chair or cradle forms. The smallest repulsions occur in the latter two. A crystal structure of $(Me_2SiNH)_4$ shows that it is actually an ordered array of chair and cradle isomers (38). The energy difference between these two forms cannot be large.

Table IV

	Si-N	Si-C	Si-N-Si	N-Si-N	N-Si-C	Ref..
$(Me_2SiNH)_3$	1.78 \pm 0.03	1.87 \pm 0.05	117 \pm 5	111 \pm 5	110	37
$(Me_2SiNH)_4$	chair 1.722	1.88	131.6	110.3	109.1	38
	cradle 1.734	1.88	132.2	111.5	108.6	
Pauling	1.73	1.94				34
Schomaker, Stevenson	1.80	1.88				34
$(H_3Si)_3N$	1.73 \pm 0.02					38

As a contrast consider the $S_4N_4F_4$ molecule, where the delocalization proposed by Craig does not occur to any considerable extent. The molecule is found by crystal structure studies (39) to be a puckered eight-membered ring with alternating S and N atoms. with F atoms attached to S. The lengths of the S-N bonds are alternately 1.55 Å and 1.65 Å. The three bonds to sulphur are in the range from a right angle to an approximate tetrahedral angle. The vacant position of the near tetrahedron is occupied by a lone pair of electrons on sulphur thus preventing the delocalization of the nitrogen lone pair. Lone pair repulsions impose a structure involving two equal tetrahedra of S and N atoms. The π system is limited to the cyclooctatetraene type with alternating bond lengths and no delocalization.

Other models have been suggested for the investigation of delocalization of the charge in rings. The S_4N_4 molecule has been of interest for many years. The accepted structure of the molecule is that of an unusual type of cage with S-N bonds of equal length and partial double bond character (40). The four nitrogen atoms form a

square plane and are surrounded by a distorted tetrahedron of sulphur atoms. An electron spin resonance investigation shows that S_4N_4 anions can be made and are consistent with delocalization involving the four equivalent nitrogen atoms (41). A free electron M.O. calculation using an electron on a sphere as a model (42) results in an ordering of energy levels which, when filled with the eight delocalized electrons in the system, verifies the diamagnetic character of the neutral molecule. The energy levels are given by the relation:

$$E = \frac{h^2 \ell(\ell+1)}{8\pi^2 \mu a^2}$$

ΔE for a spectral transition can be calculated from the above equation. The wavelength of absorption is then given by:

$$\lambda = \frac{8\pi^2 \mu a^2 c}{(2\ell+2)h} \quad \text{where } \ell \text{ is the quantum number of the highest occupied state, } l.$$

The radius of the sphere, (a), is the only parameter. Choosing (a) as 1.78\AA , the distance of the furthest atoms, N, from the center of the sphere, the value of λ for the main spectral transition is 2560\AA , in good agreement with the observed value of 2530\AA .

For the neutral molecule $\ell = 0$ and $\ell = 1$ are occupied. The wave functions are analogous in angular dependence to s and p atomic orbitals. For $\ell = 2$, the wave functions are analogous to d atomic orbitals. The form of the wave function allows a prediction of relative orders of the energy levels since the degeneracy is removed in a partially filled shell because of the differences in electronegativities. In the S_4N_4 anions, the order of filling in the $\ell = 2$ level is used to explain the observed electron spin resonance spectrum.

Conclusions

Considering the technical possibilities of inorganic polymers, one can be assured that research on inorganic rings in this sense will not lag. The increasing number of structural studies and the advent of bonding theories seem to indicate that chemists of today find rings which do not contain carbon are in themselves as interesting as those which do.

At present, the question of aromaticity in inorganic rings is not well resolved. Extreme cases are known which involved both the complete delocalization of pi-electron density as well as those where alternating single and double bonds suggest localized pi-bonding. Further experimental evidence may elucidate trends in bonding tendencies facilitating resolution of the proposed theories.

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SOME ASPECTS OF THE COORDINATION CHEMISTRY
OF 2,2-DIMETHYLAMINO-1,3-DIAMINOPROPANE

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May 19, 1964

Historical

The preparation of 2,2-diaminomethyl-1,3-diaminopropane by causing pentaerythryl tetrabromide to react with an alcoholic solution of ammonia in a sealed tube was reported by Govaert (1) in 1934. Four years later, Litherland and Mann (2) reported an improved method of synthesis for the tetraamine and indicated that a study of its complex metal salts was in progress. Whether these were coordination compounds or salts containing the cation, $[C(CH_2-NH_3)_4]^{+4}$, is not known for no further mention of this work is reported. Govaert and Beyaert (3) reported the isolation of what is the first known coordination compound of this amine. On the basis of the analyses the mercury(II) complex was formulated as $Hg_2(C_5H_{16}N_4)Cl_4$.

In 1947, Diehl (4) reported the isolation of the Schiff base, tetra (salicylidene-aminomethyl) methane, and also its cobalt(II) complex. He describes the Schiff base as being a yellow oil.

A patent (5), assigned to Du Pont De Nemours and Company by Pederson and Downing, describes the preparation of beta-ketoimine type compounds and their use to retard the transition metal ion catalyzed oxidation of organic solvents.

We considered the extension of the limited knowledge of the coordination chemistry of this amine, and also the further investigation of tetra (salicylideneaminomethyl) methane and its complexes as a legitimate extension of the study of the amine itself, to be of interest.

Experimental Results

We have prepared complexes of the amine (hereafter designated as PETA or L) and the cobalt(III), nickel(II), and copper(II) ions. All of these complexes are considered to be ionic coordination polymers of both linear and tridimensional structure.

The cobalt(III) complexes can be assigned the analytical formula, $[Co L_{1.5}]X_3$, where X is Cl^- , Br^- , I^- , NO_3^- , or SCN^- . These complexes are diamagnetic and have crystal field spectra almost identical to those of the corresponding tris ethylenediamine cobalt(III) salts.

Two nickel(II) complexes having the analytical formulae, $[Ni L_{1.5}](NO_3)_2$ and $[Ni L Cl_2]$, have been isolated and characterized. Both are paramagnetic and have crystal field spectra typical of octahedral type nickel(II) complexes. The former, as one might expect for a hexa-N-coordinated octahedral nickel(II) complex is lavender in color, while the latter is blue when fully hydrated and faint blue-green when dried for analysis.

A deep blue copper(II) complex has been formulated as $[\text{Cu L}]\text{Cl}_2$, while a light blue-green one can be written as $[\text{Cu}_2 \text{ L Cl}_4]$. Whether the latter exists as a dinuclear or a polymeric species is not known.

We have also made several attempts to prepare mixed amine complexes of the type shown in figure 1.

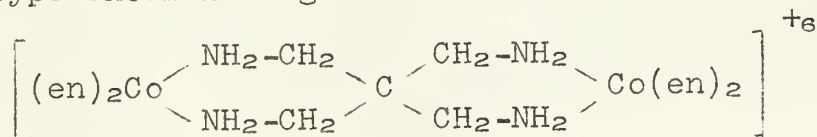


Figure 1. Bis-ethylenediamine cobalt(III)- - pentaerythryl-tetramine-bis ethylenediamine cobalt(III) ion.

However, as is frequently the case in attempts to prepare mixed amine complexes (6), dismutation takes place and tris ethylenediamine cobalt(III) ion, cobalt(II) ion and other uncharacterized products are obtained.

The Schiff base reported by Diehl (4) has been prepared by a slightly different method and found to be, not an oil, but a yellow, crystalline solid, melting near 180°C . The cobalt(II), nickel(II), copper(II), and zinc(II) complexes have been isolated and characterized. They are considered to have the structure shown in figure 2.

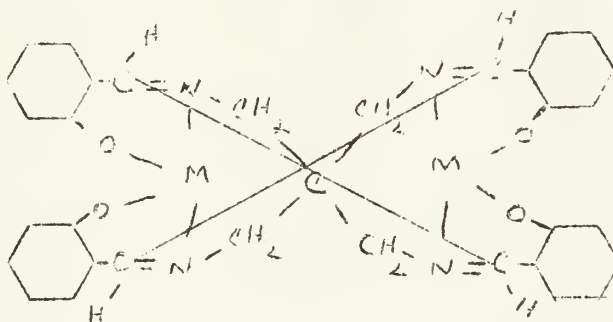


Figure 2. Tetra (Salicylideneaminomethyl) methane metal chelate complex.

The two chelate ring systems are, of course, not expected to be lying in the same plane. The complexes are soluble in D.M.F., but are quite insoluble in other common solvents. Attempts at dissolving the complexes in refluxing Xylene, benzene, or chloroform led to decomposition. The spectra in these solvents are much different from those in D.M.F. and in mineral oil mulls. The solubility properties of the complexes thus precluded any attempts at molecular weight determinations.

All, but the zinc(II) complex are paramagnetic in the solid state. The nickel complex, having a moment of 1.65 Bohr magnetons, may exist partially as an octahedral species in the crystal. The spectrum obtained is not like those for a pseudotetrahedral structure (7,8), but is more like the spectrum observed for the bis-salicylaldehyde

ethylenediimine nickel(II) complex (9). The visible band is observed at 585 mu ($\epsilon = 200$ in D.M.F.), and no band, considered diagnostic for tetrahedral nickel(II) Schiff base complexes if present, is observed in the 1,600 mu region.

The copper(II) complex exhibits only one crystal field band at about 600 mu. This type of spectrum is characteristic of planar copper(II) Schiff base complexes (10,11). A tetrahedral copper(II) Schiff base complex shows three bands in the regions 1175 mu, 740 mu, and 475 mu (10). The molar extinction coefficient (~ 500) is of the order of magnitude found for cis complexes (12).

X-ray powder patterns show that the nickel(II) and copper(II) complexes are isomorphous.

The magnetic moment of the cobalt(II) complex, 4.6 ± 0.1 Bohr Magneton, is of the magnitude assigned to tetrahedral cobalt(II) complexes (13). The electronic spectrum could be interpreted as being characteristic of a tetrahedral complex, except that a rather prominent absorption expected in the 12-15,000 mu region is not present. The complexes x-ray powder pattern does, however, resemble very closely, that of the zinc(II) complex which is not isomorphous with the nickel and copper complexes described above.

Table I - Analyses of PETA and PETS Complexes

Compound*	Calculated				Found			
	C	H	N	M ^{+x}	C	H	N	M ^{+x}
[Co L _{1.5}](NO ₃) ₃	20.32	5.43	28.50		20.84	5.77	28.86	
[Co L _{1.5}]I ₃	14.12	3.77	13.15		14.90	4.05	13.02	
[Co L _{1.5}]Cl ₃	24.8	6.63	23.15		25.23	7.45	23.20	
[Co L _{1.5}](SCN) ₃	29.38	5.58	29.38		29.95	6.14	29.50	
[Cu L]Cl ₂ ·2H ₂ O	19.85	6.62	18.50		20.38	6.63	18.12	
[Cu L]Cl ₂	22.5	6.00			22.91	6.34		
[Cu ₂ L Cl ₄]	15.0	4.02	13.95		15.57	4.03	13.56	
[Ni L _{1.5}](NO ₃) ₂ ·H ₂ O	22.6	6.5	28.1		22.72	6.31	28.01	
[Ni L _{1.5}]Cl ₂	-	-	-		-	-	-	
[Ni L Cl ₂] H ₂ O	21.41	6.48	20.02		21.51	6.88	20.41	
[Co ₂ LS]	59.5	4.23	8.46	17.8	56.30	4.65	7.99	17.4
[Ni ₂ LS]	59.70	4.23	8.47	17.8	57.92	4.50	8.58	17.35
[Cu ₂ LS]	59.0	4.18	8.34	18.9	58.53	4.01	8.11	18.84
[Zn ₂ LS]	58.84	4.15	8.29	19.34	58.39	4.55	7.30	20.84

L = C(CH₂-NH₂)₄

LS = C(CH₂-N=CH-C₆H₄OH)₄

Table II - Spectral Data on PETA Complexes in Water

Complex	λ max (in m μ .)	ϵ molar
[Co L _{1.5}]Cl ₃	466 338	68 65
[Co L _{1.5}](NO ₃) ₃	468 (340)	68 (69)
[Co(en) ₃]Cl ₃	475 336	75 80
[Cu L]Cl ₂	575	84
[Cu tn ₂]Cl ₂	568	111
[Cu ₂ L(H ₂ O) ₄]Cl ₄	660	91.5
[Cu en(H ₂ O) ₂]SO ₄	652	--
[Ni L _{1.5}]Cl ₂	855 (760) 522 335	15.8 -- 14.2 16.6
[Ni L (H ₂ O) ₂]Cl ₂	989 (770) 598 360	22.9 -- 16.7 20.8

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THE THERMAL DECOMPOSITION OF POTASSIUM CHLORATE

Spring of 1964

R.F. Trimble

Introduction.

KClO_3 was first reported by Berthollet (1) in 1786. Note was made that it loses oxygen on heating. Serullas (2) reported in 1831 that KClO_4 was formed when KClO_3 was heated and that the total amount of oxygen was not liberated at temperatures below the decomposition point of KClO_4 ($\approx 500^\circ$). In 1832 Döbereiner (3) observed the catalytic action of MnO_2 and found that no KClO_4 was formed in the catalyzed decomposition. Marignac (4) in 1842 and Erdmann and Marchand (5) in 1844 commented on the formation of Cl_2 in the uncatalyzed and catalyzed decomposition, respectively.

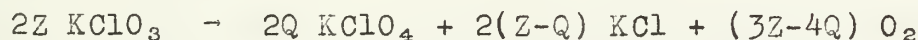
Uncatalyzed Decomposition.

A. The melting point of KClO_3 is probably close to 357° (6-9) although other, widely different values have been reported.

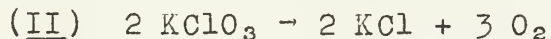
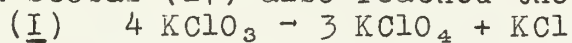
B. The temperature at which the decomposition begins has been variously reported to be: 500° (9), 495° (10), $440 \pm 5^\circ$ (11), 365° (12), 364° (8), and 223° (13). The last value was observed with a single crystal on a microscope stage. Decomposition started only after 6 hours and proceeded from nuclei on the crystal faces. The products are not given. Light contact or prior rubbing with MnO_2 did not hasten decomposition.

Over the temperature range $330-400^\circ$ 2g. of KClO_3 evolved O_2 at a rate of 1cc/min. (14)

C. The stoichiometry of the reaction was long in being established. Marignac (4) first suggested the reactions leading to KClO_4 and to O_2 to be independent. Bottomly (15) showed that the equation



was balanced for any pair of integers Z and Q so long as $Z > (4/3)Q$. Sodeau (16) and Scobai (17) also reached the conclusion that the reactions:



are independent. They do not reach equilibrium. ΔF° is -38 kcal/ for I and -56 kcal for II. The equilibrium pressure of O_2 in II would be 10^{16} atmospheres.

D. The rate of decomposition has been measured and mechanisms for the reaction proposed. Scobai (17) reported that I was 4th order and II was 1st order in molten KClO_3 at 395° and also in molten KNO_3 solution at 410° . Reaction I was catalyzed by KCl . This work was criticized by Otto and Fry (18) on several grounds

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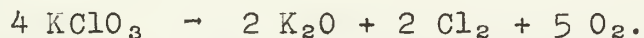
but they also found that I was autocatalytic and that II was 1st order at 409 to 506°. Glasner and Weidenfeld (19) report that II appears to be 1st order above 527°. The effect of KCl on I depended on its history. KCl dried at 110° for 2 hours retarded KClO₄ formation whereas KCl dried at 600° for an hour accelerated it. They conclude that I and II are consecutive reactions rather than simultaneous ones and that KCl is attacked by active O to form KClO₄. However, both van den Bosch and Aten (20) and Brown and Woods (21) found no Cl exchange between ³⁶Cl⁻ and ClO₄⁻ or ClO₃⁻ during the decomposition of KClO₃.

Osada (22) claims to have found KClO₂ among the intermediate decomposition products so that the reaction proceeds:



Tobisawa (9) studied the decomposition at 565-575° and found that the weight loss vs. time curves were too complicated for a rate to be deduced from them.

E. Some chlorine is also liberated during the decomposition. Marignac found (51) that 50g. of KClO₃ gave 3mg. of AgCl. Sodeau (16) found that 1g. of KClO₃ in a Pt vessel at 400° released 0.002% of its Cl as free Cl₂. This amount was the same at both 1 and 760 mm of Hg total pressure. In glass vessels, however, the figure rose to 0.01 - 0.02%. Sodeau (23) considered various reactions proposed to explain the appearance of Cl₂ (24, 46) and on the basis of his results in the decomposition of several different chlorates concluded that the Cl₂ results from the reaction:



This mode of decomposition is much more important for Pb(ClO₃)₂ and AgClO₃ than for KClO₃ or Ba(ClO₃)₂.

Catalyzed Decomposition.

A. A large number of substances have been found to catalyze reaction II (26). Different criteria for catalytic effectiveness and different experimental conditions make it difficult or impossible to compare the results of different studies. In general transition metal compounds, particularly the oxides, are the most effective. Kolhatkar and Sant (27) found the volume of O₂ produced in 30min. at 275° to decrease with the following order of catalysts: Co₂O₃ > Cr₂O₃ > MnO₂ > Fe₂O₃ > Ni₂O₃ > CuO > TiO₂. For the sulfates they observed the series Fe(II) > Co(II) > Ni(II) > Cu(II). Vanadium Chloride was less effective than CuSO₄. Solymosi and Krix (41) found the activation energy of the decomposition to decrease in the series: MgO > ZnO > TiO₂ > CuO > NiO.

In what follows we shall concern ourselves primarily with the role of MnO₂.

B. The effectiveness of MnO_2 as a catalyst is not diminished by repeated use although its appearance is changed (6). Fukushima (28) has shown that O is exchanged between $\text{KCl}^{18}\text{O}_3$ and MnO_2 during the decomposition and that only part of the MnO_2 is catalytically active. This has been confirmed by Brown and Woods (29) with KClO_3 and Mn^{18}O_2 . They estimate only 20% of the catalyst was active in a 1:1 mole mixture.

The effectiveness of MnO_2 depends on its mode of preparation and its prior treatment (28,30). Balerov (31) showed that moistening the reaction mixture or compressing it with a stirring rod led to the evolution of O_2 at a lower temperature.

It has been (32) found that each mixture of KClO_3 and MnO_2 has a particular decomposition temperature which depends on the composition of the mixture and the pressure. A minimum temperature (at 1 atm.) of 295° was obtained with a 2:1 KClO_3 to MnO_2 mole ratio. For any temperature there was a pressure above which the decomposition was slow or absent (33). A 2:1 mixture evolved O_2 at 125° when the pressure was less than 0.1 mm of Hg, at 175° for 2-3 mm of Hg. At 300° and 1 atm. the decomposition was almost explosive but at 320° and a pressure in excess of 300 atm. the mixture was 90% undecomposed after 7 hours. There was a continuous decomposition at 68° when the pressure was sufficiently low. Balerov (31) found no trace of Cl^- in a mixture of KClO_3 and MnO_2 that had been kept at room temperature for a year whereas there was a large amount of Cl^- in such a mixture after an hour at 140° . There was no KClO_3 found in a mixture of KCl and MnO_2 after 7 days at 145° and 100 atm. of O_2 (33).

C. The formation of KMnO_4 during the decomposition has frequently been noted (6, 16, 34, 35) although Miravet and Rocchiccoli (11) failed to find any infrared absorptions due to MnO_4^- among the reaction products. The formation of KMnO_4 has been assumed to be vital part of the mechanism of the catalyzed decomposition, however, KMnO_4 itself is not as effective as MnO_2 in lowering the decomposition temperature (6, 34). On the other hand, Yamamoto and Asaba (36) found no difference in the kinetic behavior of the decomposition catalyzed by MnO_2 , KMnO_4 , or K_2MnO_4 . They report the reaction to be 1st order in KClO_3 and in catalyst above 380° , the melting point (sic) of KClO_3 .

Brown (35) points out that whereas MnO_2 does not lose its effectiveness with use, rhenium catalysts are converted completely to ReO_4^- and do not exhibit continuous activity. This is interpreted to mean that the cyclic oxidation-reduction of the catalyst is essential to its activity. KMnO_4 decomposes at 240° and lower valence Mn compounds are regenerated but the formation of KReO_4 , which can be distilled without decomposition at 1370° , brings an end to the catalytic activity of the Re.

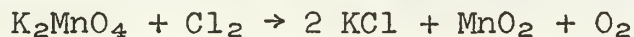
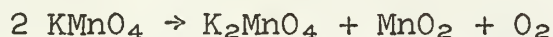
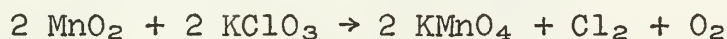
D. A study of the magnetic susceptibilities of partly decomposed KClO_3 - MnO_2 mixtures showed that during the intermediate stages of the reaction the measured magnetic susceptibility was less paramagnetic than that calculated for the appropriate mixture of

KClO₃, KCl, and MnO₂. There was no such discrepancy with the initial mixture and the final, completely decomposed one (37). Similar behavior was observed with Co₃O₄ but not with Fe₂O₃ (38).

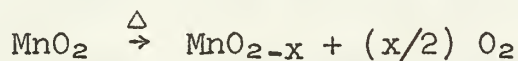
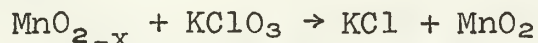
The statement that Fe₂O₃ acts as a promoter for MnO₂, enhancing its catalytic activity (39) has been subjected to a detailed study and rejected (32).

E. The decomposition is accompanied by the formation of varying amounts of Cl₂ (42-46, 6). Sodeau showed that the amount of Cl₂ was not increased by carrying out the decomposition under reduced pressure (44). This would seem to indicate that the Cl₂ was not formed in large quantity by a primary reaction and then recombined. Brunck (47, 48) claimed that what was reported to be Cl₂ was in fact a form of ozone. In support of this, he pointed out that the gas reacted with neutral KI solution to form I₂ and OH⁻, oxidized alcohol to aldehyde, was not absorbed by KOH solution, and that the odor and oxidizing power were lost when the gas was led over a layer of MnO₂ at room temperature. He cited as contrary evidence the facts that the color was greenish yellow, that it did not attack Hg, that it seemed to have greater thermal stability than regular O₃, and that it did not attack organic materials such as rubber as readily as O₃. McLeod (42, 43) contested the identification of the gas as O₃ instead of Cl₂. Recently, Gaidis (49) has presented evidence that ClO₂ may be formed during the decomposition. This would explain the peculiarities which led Brunck to postulate a greenish modification of ozone.

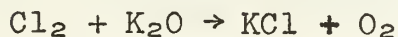
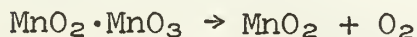
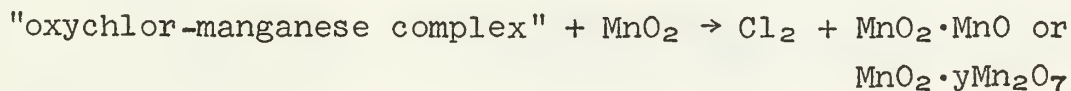
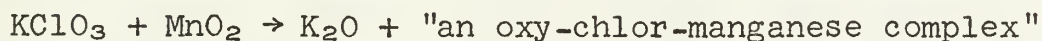
F. A number of mechanisms have been proposed but no one of them seems adequate to explain all of the observed facts. McLeod (6) has suggested the sequence:



Veley (50) pointed out that MnO₂ never has the stoichiometric composition but is always oxygen deficient and suggested:



On the basis of their magnetic studies, Bhatnagar and his colleagues (37) proposed the sequence of reactions:



1. The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function and that its value is zero.

2. In the second part of the paper, we consider the function $g(x)$ defined by the equation $g(x) = \int_0^x g(t) dt$. It is shown that $g(x)$ is a constant function and that its value is zero.

3. The third part of the paper is devoted to the study of the properties of the function $h(x)$ defined by the equation $h(x) = \int_0^x h(t) dt$. It is shown that $h(x)$ is a constant function and that its value is zero.

4. In the fourth part of the paper, we consider the function $k(x)$ defined by the equation $k(x) = \int_0^x k(t) dt$. It is shown that $k(x)$ is a constant function and that its value is zero.

5. The fifth part of the paper is devoted to the study of the properties of the function $l(x)$ defined by the equation $l(x) = \int_0^x l(t) dt$. It is shown that $l(x)$ is a constant function and that its value is zero.

6. In the sixth part of the paper, we consider the function $m(x)$ defined by the equation $m(x) = \int_0^x m(t) dt$. It is shown that $m(x)$ is a constant function and that its value is zero.

7. The seventh part of the paper is devoted to the study of the properties of the function $n(x)$ defined by the equation $n(x) = \int_0^x n(t) dt$. It is shown that $n(x)$ is a constant function and that its value is zero.

8. In the eighth part of the paper, we consider the function $o(x)$ defined by the equation $o(x) = \int_0^x o(t) dt$. It is shown that $o(x)$ is a constant function and that its value is zero.

9. The ninth part of the paper is devoted to the study of the properties of the function $p(x)$ defined by the equation $p(x) = \int_0^x p(t) dt$. It is shown that $p(x)$ is a constant function and that its value is zero.

10. In the tenth part of the paper, we consider the function $q(x)$ defined by the equation $q(x) = \int_0^x q(t) dt$. It is shown that $q(x)$ is a constant function and that its value is zero.

11. The eleventh part of the paper is devoted to the study of the properties of the function $r(x)$ defined by the equation $r(x) = \int_0^x r(t) dt$. It is shown that $r(x)$ is a constant function and that its value is zero.

$$\begin{aligned} f(x) &= \int_0^x f(t) dt \\ g(x) &= \int_0^x g(t) dt \\ h(x) &= \int_0^x h(t) dt \end{aligned}$$

12. The twelfth part of the paper is devoted to the study of the properties of the function $s(x)$ defined by the equation $s(x) = \int_0^x s(t) dt$. It is shown that $s(x)$ is a constant function and that its value is zero.

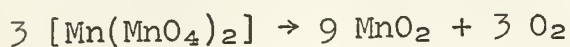
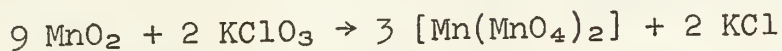
$$\begin{aligned} i(x) &= \int_0^x i(t) dt \\ j(x) &= \int_0^x j(t) dt \end{aligned}$$

13. The thirteenth part of the paper is devoted to the study of the properties of the function $t(x)$ defined by the equation $t(x) = \int_0^x t(t) dt$. It is shown that $t(x)$ is a constant function and that its value is zero.

$$\begin{aligned} u(x) &= \int_0^x u(t) dt \\ v(x) &= \int_0^x v(t) dt \end{aligned}$$

$$\begin{aligned} w(x) &= \int_0^x w(t) dt \\ x(x) &= \int_0^x x(t) dt \end{aligned}$$

Deniges (34) thought that the low activity of KMnO_4 precluded its being of fundamental importance in the decomposition and that the catalysis proceeded via:



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